

# THE RADIATION CHEMISTRY OF ORGANIC SUBSTANCES

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## CONTENTS

I. Introduction.....	473
II. Aliphatic compounds.....	477
A. Saturated hydrocarbons.....	477
1. Mixtures with other substances.....	477
2. Pure hydrocarbons.....	478
(a) Reactions in the vapor phase.....	478
(b) Reactions in condensed phases.....	478
B. Unsaturated hydrocarbons.....	479
1. Pure acetylenic hydrocarbons.....	480
2. Pure ethylenic hydrocarbons.....	481
3. Dienes.....	482
4. Mixtures with other substances.....	483
C. Vinyl compounds.....	484
1. Mixtures with other substances.....	484
2. Pure monomers in the liquid phase.....	486
3. Polymerizations in the solid phase.....	487
4. Polymerizations in the vapor phase.....	488
D. Halides.....	488
1. The radiosensitivity of the halides.....	488
2. Chlorides.....	489
3. Bromides.....	490
4. Iodides.....	490
5. Dosimetry.....	491
E. Alcohols, hydroxy acids, and carbohydrates.....	492
1. Alcohols.....	492
2. Hydroxy acids.....	493
3. Carbohydrates.....	493
F. Aldehydes and ketones.....	494
G. Carboxylic acids and their esters.....	494
1. Pure acids and esters.....	494
2. Aqueous solutions.....	495
(a) Formic acid.....	495
(b) Other acids.....	497
H. Nitrogen-containing compounds.....	498
1. Quaternary ammonium compounds.....	498
2. Other compounds.....	498

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III. Aromatic compounds.....	499
A. Hydrocarbons.....	499
1. Mixtures with similar hydrocarbons and with other substances.....	500
(a) Free-radical yields.....	500
(b) Hydrocarbon mixtures.....	500
(c) Mixtures with other organic compounds.....	502
(d) The mechanism of intermolecular energy transfer.....	503
(e) Mixtures with water.....	505
(f) Halogenation.....	507
(g) Other mixtures.....	508
2. Pure hydrocarbons.....	508
(a) Benzene.....	508
(b) Other hydrocarbons.....	510
B. Other compounds.....	512
1. Pure compounds.....	512
2. Non-aqueous mixtures.....	513
3. Mixtures with water.....	514
IV. Polymers.....	517
A. Vinyl polymers.....	517
1. Polyethylene and related materials.....	518
2. Polystyrene.....	521
3. Polymethyl methacrylate.....	521
4. Polyvinyl chloride.....	521
5. Polytetrafluoroethylene.....	521
6. Other vinyl polymers.....	521
B. Other types of polymer.....	522
C. Polymers in the presence of oxygen.....	522
D. Polymers in solution.....	523
V. Organic oxidation-reduction systems and dyes.....	524
A. Aqueous solutions.....	525
1. The effect of oxygen.....	525
2. Methylene blue.....	525
3. Xanthenes.....	527
4. Other dyes.....	527
B. Aqueous solutions with other substances present.....	528
C. Non-aqueous solutions.....	529
VI. Substances of biochemical interest.....	529
A. Steroids.....	529
1. General.....	529
2. Cholesterol.....	536
B. Amino acids.....	537
1. General.....	537
2. Glycine.....	537
3. Alanine.....	538
4. Serine.....	538
5. Tyrosine.....	538
6. Histidine.....	539
7. Miscellaneous amino acids.....	539
C. Thiols and disulfides.....	539
1. The oxidation of thiols.....	539
2. Minor reactions.....	540
3. Disulfides.....	540
D. Proteins.....	540
1. Direct action.....	540

2. The inactivation of enzymes in aqueous solution.....	541
(a) The effect of linear energy transfer.....	541
(b) The effect of enzyme concentration.....	541
(c) The effect of other irradiation conditions.....	541
(d) The after-effect.....	542
(e) The mechanism of inactivation.....	542
(f) The protective effect.....	542
(g) Use of the protective effect in determining reaction mechanism.....	543
3. Sensitive groups in the protein.....	544
4. Changes in physicochemical properties of proteins.....	544
(a) Electrophoretic changes.....	544
(b) Changes in absorption spectrum.....	545
(c) Changes in molecular weight.....	545
5. The inactivation of toxins.....	545
E. Vitamins, coenzymes, and respiratory proteins.....	545
1. General.....	545
2. Nicotinic acid.....	546
3. Coenzyme I.....	546
4. Thiamine.....	547
5. <i>p</i> -Aminobenzoic acid.....	547
6. Ascorbic acid.....	547
7. Auxin.....	547
8. Cytochrome c.....	547
9. Hemoglobin.....	548
10. Hemocyanin.....	548
F. Polysaccharides.....	548
1. Aqueous solutions.....	548
2. Dry polysaccharides.....	548
G. Nucleic acids and related compounds.....	549
1. Dry nucleic acids.....	549
2. Solutions of nucleoproteins.....	549
3. Changes in viscosity of nucleic acid solutions.....	549
4. Other physicochemical changes in nucleic acid solutions.....	550
5. Entities responsible for the viscosity effects.....	550
6. Chemical changes in nucleic acid solutions.....	551
7. Labile phosphate esters.....	552
VII. Future possibilities.....	552
VIII. References.....	553

## I. INTRODUCTION

As long ago as 1895 Roentgen observed the blackening of a photographic plate by x-rays. A few months later Becquerel reported that the same chemical change could be brought about by the previously unsuspected radiation from a uranium salt. Yet radiation chemistry is still very much in its infancy. This is especially true of the radiation chemistry of organic substances, since much of the work so far published on this topic is incomplete, and empirical in approach. The currently increasing availability of nuclear fission products not only provides for further study but at the same time creates a need for it, since it is desirable to develop every conceivable practical use for these commodities. Hence it seems timely to review the present state of our knowledge in this field.

In the broadest sense radiation chemistry includes photochemistry, the

chemistry of reactions occurring in electric discharges, and the chemistry of changes in the atomic nucleus brought about by neutrons and radiations of very high energy. In the present review none of these branches will be considered, and the subject will be taken to include only reactions induced by x- and  $\gamma$ -rays, electrons produced in machines and  $\beta$ -particles from nuclear disintegration, protons, deuterons,  $\alpha$ -particles, and neutrons, giving rise to extranuclear changes.

Of specific interest in radiation chemistry are (a) the reactive entities initially produced by the radiation concerned, and (b) the way in which these are distributed. The most obvious property of ionizing radiations being the production of ions, it was thought for many years that ions were the sole precursors of the observed chemical effects. This concept had its origin in the fact that for several gaseous reactions the number of molecules reacting ( $M$ ) was approximately the same as the number of ions ( $N$ ) formed in the gas in the same time. Consequently the quantity  $M/N$ , the ionic yield, was regarded as being the radiation-chemical equivalent of the photochemical quantum yield. When it was realized that ionic yields were often greater than the corresponding quantum yield, the difficulty was met by the "Cluster Hypothesis." On this concept several molecules were considered to cluster around each ion, there being some physical evidence for the occurrence of this phenomenon in gases. Chemical breakdown of the cluster as a whole took place on its being neutralized by an ion or a cluster of opposite charge. However, since the average energy to form an ion pair ( $W$ ) for a gas is generally in the region of 26–38 e.v., whilst the first ionization potential ( $I$ ) is about 9–15 e.v., it might be expected that the excess energy ( $W - I$ ) could be used to form chemically reactive species other than ions. In two, now classic, papers (213, 214) earlier work on the  $\alpha$ -particle-induced ortho-para hydrogen conversion and on the synthesis and decomposition of hydrogen bromide was interpreted on this basis. Moreover, the study of gaseous reactions with and without the application of an electric field lent support to the view that uncharged entities play a significant part in the chemical processes (212). In consequence it is now accepted that both ions and excited molecules may play an active part, but there are few data available regarding the exact nature of these entities in any given case. The process of ionization may or may not be accompanied by dissociation or rearrangement, and some information on this question may be obtained from mass spectrometric observations. Nevertheless such results can only be regarded as *possible* indications of what will occur in irradiated systems, where conditions will generally be very different from the rather special ones obtaining in the mass spectrometer (86, 489).

All ionizing radiations ultimately transfer energy to an irradiated system via particles. In the case of x-rays or  $\gamma$ -rays, the effective particles are high-energy electrons ejected by the interaction of photons with atoms. Theoretical analysis indicates that fast charged particles, in addition to effecting ionization of the atoms with which they interact, cause excitation through optically allowed transitions, mainly to the lowest allowed excited state. Such processes correspond exactly to those of the photochemical primary act. On the other hand, slow secondary electrons (of energy 20–100 e.v.) may give rise to excited states

differing in multiplicity from the ground state, i.e., by optically "forbidden" transitions. Other, generally less effective, primary processes may arise from nuclear collisions (particularly effective where neutrons impinge on molecules containing hydrogen atoms), Auger disruptions, and multiple ionizations (479), but usually these effects are negligible.

After the formation of the primary ions and excited molecules, a variety of secondary processes may occur before any ultimate chemical change results. Among the possibilities for which there is evidence are transfer of excitation and ionization between like or unlike molecules, neutralization of ions, and formation of negative ions, all with or without decomposition to radicals or molecules, and also the disruption of excited molecules to radicals or new molecules. The effect of state on these secondary processes may be quite marked, and in condensed systems the situation is more complex and less well understood. It seems likely, however, that in the liquid phase both the increased collision rate and the Franck-Rabinowitch cage effect will favor breakdown to molecular products rather than to radicals: the former by increasing the probability of energy removal before decomposition; the latter by tending to cause recombination of radicals once formed.

The distribution of the new entities produced by irradiation, whether radicals or ions, will depend on the type of particle generating them and on its energy. The energy lost by a particle per unit length of its path has been termed its "linear energy transfer" (L.E.T.) (637). This quantity (also known as the "stopping power," "specific ionization," or "track density") increases with increasing charge on the particle and with decreasing velocity. As might be expected, the difference in proximity of the entities produced in the track of, say, an  $\alpha$ -particle or an electron may lead to a difference in the ultimate chemical response of the system. Such effects are commonly observed in aqueous systems, and a few cases are known from investigations on organic materials. The term "linear energy transfer" should not be confused with the term "energy transfer," which is applied to the transfer of ionization or excitation energy from one molecule to another, or from one part of a molecule to another part of the same molecule.

Owing to the difficulties attending ionization measurements in liquids, ionic yields can only be obtained with accuracy for gas reactions. Consequently it is now common practice to express yields in terms of the energy yield,  $G$ . This is the number of molecules produced in a given reaction for each 100 e.v. of energy absorbed. The material produced is written in brackets, and the radiation is written as a subscript. Thus  $G_{\alpha}(A) = 2$  means that in a certain reaction induced by  $\alpha$ -particle irradiation, two molecules of A are produced for each 100 e.v. of energy absorbed. If in another reaction induced by x-ray irradiation A disappeared at the same rate, we should write  $-G_x(A) = 2$ . A commonly employed method for measuring the rate of energy absorption, or dose rate, in dilute aqueous solutions or systems of equivalent electron density is to use the ferrous sulfate dosimeter. The yield of oxidation of ferrous sulfate in 0.8 *N* sulfuric acid

is known for several radiations, and a measurement of the rate of oxidation in this system, under the proposed experimental conditions, enables the dose rate to be calculated. The value of the yield for  $\gamma$ -rays and hard x-rays is now believed to be  $G_{\gamma}(\text{Fe}^{3+}) = 15.5$ , but other values have often been employed in previous work. In cases where workers have used this method of dosimetry the authors of this review have normalized the energy yields given to  $G_{\gamma}(\text{Fe}^{3+}) = 15.5$ .

Organic materials have been irradiated both pure and as mixtures. The commonest types of mixture to be investigated are those with oxygen, with water, or with both. In many cases the presence of oxygen leads to results completely different from those obtained with the pure substance, an effect probably to be associated with the high electron affinity of oxygen. The study of dilute solutions of one substance in another introduces the concept of *indirect action*. This arises from the non-specificity of absorption of the energy of ionizing radiations, from which it follows that if material A is present in very much greater quantity than material B, as in a dilute solution, then A will absorb most of the radiation energy, and chemical effects on B are more likely to arise via the primary entities formed from A than from a direct effect of the radiation on B. In dilute air-free aqueous solutions, it is found that very many of the reactions induced by ionizing radiations in the solutes can be explained on the assumption that the reactive entities formed from water are hydrogen atoms and hydroxyl radicals, and that these react with the solutes. The yields of these radicals are denoted by  $G^R(\text{H})$  and  $G^R(\text{OH})$ . Molecular products—hydrogen and hydrogen peroxide—are also formed in water, the yields being denoted by  $G^M(\text{H}_2)$  and  $G^M(\text{H}_2\text{O}_2)$ . In aerated aqueous solutions hydrogen atoms are believed to react with oxygen as follows:



In acid solutions the reducing hydrogen atom is thus converted to an oxidizing entity. In alkaline or neutral solutions the effective reaction becomes



and  $\text{O}_2^-$  may behave as a reducing agent.

Owing to the phenomenon of indirect action the change brought about in any solute which is an efficient "radical catcher" may be used as a measure of the yield of radicals from a solvent. Solute which have been used for this purpose in organic systems include vinyl monomers and diphenylpicrylhydrazyl (67, 110, 111, 489, 545). The methods give useful comparative results, but, as instanced by the discrepancies between the results of different workers, the absolute yields obtained are at present suspect. There are several possible reasons for this. Probably the most fundamental objection to both methods is the possibility of energy transfer from the solvent to the solute, where conditions are suitable for such an occurrence, giving a solute reaction and so increasing the apparent radical yield of the solvent. Other objections to the diphenylpicrylhydrazyl (DPPH) technique have been raised (625), among which may be included the possible disruption of some DPPH molecules as opposed to radical addition, the effect of solvation of DPPH, and the inefficiency of DPPH as a radical scavenger

(56), all tending to reduce the apparent radical yield. The use of vinyl compounds in this connection is discussed under that heading.

In a recent review of the radiation decomposition of pure organic compounds (609) a number of tables of energy yields for pure materials have been presented. These data are not repeated in this review, but other quantitative results, notably on mixtures, are summarized. Several articles and books dealing with general topics in radiation chemistry are available (25, 85, 163, 363).

## II. ALIPHATIC COMPOUNDS

### A. SATURATED HYDROCARBONS

Most of the work on hydrocarbons has been with  $\alpha$ -particles, deuterons, and other densely ionizing radiations, but there has been some work with electrons. In contrast to other examples in radiation chemistry, notably aqueous solutions, there seems to be little or no difference between the effects produced by the various kinds of radiation. A direct comparison has been made for cyclohexane. Electrons of energy 2 m.e.v., 14 m.e.v. deuterons, and 35 m.e.v.  $\alpha$ -particles were all shown to produce the same energy yield of hydrogen (537).

Several attempts have been made to correlate the radiation chemistry of hydrocarbons with mass spectroscopic data (84, 410, 466, 611, 614), but it is not yet possible to predict radiation-chemical changes from such data.

#### 1. *Mixtures with other substances*

Both C—C and C—H bonds can be broken when hydrocarbons are irradiated, and the highly reactive fragments formed are capable of a variety of reactions, including reaction with each other. If a foreign substance is present, the fragments are likely to react with it, especially if it is a good acceptor. A useful approach to the problem of elucidating the number of carbon atoms in the reactive fragments has been to mix radioactive iodine with the hydrocarbon. Alkyl iodides are formed and these can be identified. By this method it was found that methane gives methyl iodide and methylene diiodide, while ethane gives ethyl iodide, methyl iodide, and ethylene diiodide. The iodides formed from normal hydrocarbons always have either the same number of carbon atoms as the original or less, and no high degree of specificity is apparent (253, 627). So far, however, the data provide insufficient basis for generalization. Surprisingly, it was found that for cyclohexane and 2,2,4-trimethylpentane with iodine present, the yield of hydrogen and methane is the same as in the absence of iodine (536). With high concentrations of iodine the gas yield even increases, owing to increased absorption of energy by the system.

It was found that oxygen interferes with the consumption of iodine during the action of radiation on *n*-heptane (227), a result which shows that oxygen is also a good acceptor for the reactive fragments or their precursors. The readiness with which oxygen reacts is evident in the radiation chemistry of methane and ethane. With oxygen present, water and the oxides of carbon are produced, and the ordinary synthetic and degradative processes are suppressed (377, 379, 426). To some extent this is also true for higher hydrocarbons. One important reaction

of hydrocarbons in the presence of oxygen is the formation of peroxides (23, 268).

Methane is the only saturated hydrocarbon that has been irradiated in aqueous solution. Formaldehyde is formed in acid solution when oxygen is present, and in neutral solution methyl hydroperoxide is also formed (319).

## 2. Pure hydrocarbons

When no foreign substance is present, the reactive fragments can react with each other or with the original material. As both carbon-carbon and carbon-hydrogen bonds are broken, the products formed are hydrogen and hydrocarbons of both lower and higher molecular weight than the original. The primary ionization and excitation must be independent of the physical state of the system, but the reactions of the ions and excited molecules are not, and differences have been observed depending on the phase. In the liquid phase the formation of hydrogen and lower hydrocarbons appears to be less than in the vapor phase, possibly owing to collisional deactivation processes or to a greater extent of radical recombination within the "cage" (295).

### (a) Reactions in the vapor phase

In contrast to much of the work in radiation chemistry, large doses have often been used to irradiate hydrocarbons, so that the initial products are also changed. Thus, when methane is irradiated, the first result is the formation of hydrogen and ethane (377, 426) in the overall process:



N. On longer irradiation the ethane itself is attacked, higher hydrocarbons are formed, and ultimately a liquid product appears (306, 379). Ethane, as expected, gives a liquid product more quickly than methane (376, 377, 458), and methane is also produced (306, 377, 379). Similar results have been found for higher hydrocarbons (295, 306, 377, 379). There are no unsaturated hydrocarbons in the vapor phase after irradiation, but the condensed products are partly unsaturated (295, 306) and may also be partly cross-linked (130). The results have been interpreted on the supposition that the probability of carbon-carbon to carbon-hydrogen breaks is 0.36, and that when carbon-carbon bonds are broken the fragments are saturated to give lower hydrocarbons, whereas when carbon-hydrogen bonds are broken the fragments join together or react with unchanged hydrocarbon to give cross-linked molecules of higher molecular weight (130).

### (b) Reactions in condensed phases

For straight-chain hydrocarbons it was found that the hydrogen yield from the simultaneous irradiation of both the vapor and the liquid phases increases with molecular weight, and the methane yield decreases (525). This is explicable on the "statistical principle" (85), which in this case would predict that the ratio of methane to hydrogen would depend on the ratio of methyl groups to hydrogen



atoms, i.e., it would decrease with chain length. The results of irradiating branched-chain hydrocarbons are also in agreement with this principle, for the methane yield increases in the order *n*-octane < 2,5-dimethylhexane < 2,2,4-trimethylpentane.

It might be expected that long-chain hydrocarbons irradiated in the condensed phase would give the same products as lower hydrocarbons irradiated in the vapor phase, i.e., hydrogen and lower and higher hydrocarbons. The yields would not necessarily be the same, owing to the greater likelihood of collisional deactivation and cage recombination. In one investigation however, hydrogen and some gaseous hydrocarbons were found, but the expected non-volatile hydrocarbons of lower molecular weight than the original could not be detected (72). The reason is not clear.

The higher hydrocarbons formed from paraffins irradiated in the condensed phase absorb oxygen from the air, so they must have a degree of unsaturation (524a). However, the carbon:hydrogen ratio is found to be very much greater than that of the original hydrocarbon, and the main reason is probably that the product is cross-linked (130). In support of this view it is found that the melting point of the hydrocarbons at first decreases on irradiation, owing to the presence of miscellaneous irradiation products, but ultimately rises steeply, owing to the formation of an infusible and insoluble gel.

#### B. UNSATURATED HYDROCARBONS

Information regarding the primary act in the irradiation of these substances is limited, but it seems clear from mass spectrometric observations that (i) multiple bonds are not themselves broken and they inhibit the rupture of neighboring single bonds, (ii) triple bonds are more effective in this respect than double bonds, and two double bonds are more effective than one, (iii) the effect of a multiple bond is least marked when at the end of a chain, and (iv) the *cis* form of an ethylenic compound is broken down more readily than the *trans* form (466, 611). In general accord with (i) and (iii) it is found that the radiation yields of gaseous products are less, whilst the total yields and the yields of polymeric products are greater, from unsaturated than from the corresponding saturated hydrocarbons (284, 285, 286, 287, 288), and that polymerization yields are higher for molecules which have a multiple bond at the end of the chain than for those which have a like bond in other positions (132).

Though the principal reaction of unsaturated hydrocarbons on irradiation is polymerization, the mechanism is not always clear. The low yields of gaseous products may possibly be caused by the removal of gas-producing radicals as they are formed, in polymerization or other reactions with multiple bonds. This explanation receives support from the fact that the evolved gas generally contains a lower proportion of hydrogen than that from saturated hydrocarbons, whereas mass spectrometric results show that the presence of a multiple bond increases the proportion of fragments with simple loss of a hydrogen atom (410). Nevertheless it would be wrong to assume that the radicals so absorbed were necessarily used to initiate a free-radical chain reaction of the type encountered

TABLE 1

*Radiation yields from unsaturated aliphatic hydrocarbons at normal temperatures and pressures*  
 $G(\text{total}) \simeq G(\text{polymer}) \simeq G(\text{cross-link})$

Substance	Radiation	$G(\text{total})$	$G(\text{polymer})$	$G$ (cross-link)	Reference
Methylacetylene.....	Radon $\alpha$	29.7			(284)
Dimethylacetylene.....	Radon $\alpha$	20.7			(284)
1-Decyne.....	Pile			14.3	(132)
1-Heptadecyne.....	Pile			18.3	(132)
1-Octadecyne.....	Pile			17.0	(132)
9-Octacosyne.....	Pile			17.4	(132)
11-Docosyne.....	Pile			7.1	(132)
16-Dotriacontyne.....	Pile			8.4	(132)
Propylene.....	Radon $\alpha$	17.5			(285)
Isobutylene.....	Radon $\alpha$	$\begin{Bmatrix} 159^* \\ 393^\dagger \end{Bmatrix}$			(456)
2-Butene.....	Radon $\alpha$	13.6			(284)
1-Decene.....	Pile			10.9	(132)
1-Octadecene.....	Pile			10.3	(132)
9-Octadecene ( <i>trans</i> ).....	Pile			6.1	(132)
9-Octadecene ( <i>cis</i> ).....	Pile			6.4	(132)
Cyclobutene.....	Radon $\alpha$	26.4			(288)
Cyclopentene.....	Radon $\alpha$	16.1			(287)
Cyclohexene.....	1.5 m.e.v. electrons		12.4		(412)
Allene.....	Radon $\alpha$	38			(284)
Isoprene.....	Radon $\alpha$	45			(284)
2,5-Dimethyl-1,5-hexadiene.....	Pile			13.9	(132)
Vinylacetylene.....	Radon $\alpha$	41			(286)

\* At 304°A.    † At 273°A.

in vinyl polymerizations. The polymer yield may be large enough to indicate quite clearly a chain mechanism, as is the case with isobutylene or with ethylene at high pressures (see below), but such examples are rare, and in most cases even the overall yields are low enough to be explained without recourse to a chain mechanism (see table 1). It has been suggested that the presence of a multiple bond serves to increase the rate of condensation or cross-linking, but that chain reactions do not occur (132).

### 1. Pure acetylenic hydrocarbons

The effects of the  $\alpha$ -particle irradiation of methylacetylene, dimethylacetylene (284), acetylene itself (371, 459, 462, 509, 510), and deuterioacetylene (382) have been studied. Acetylene has also been irradiated with electrons (257, 428)  $\beta$ -particles (457, 459), and  $\gamma$ -rays (74, 76, 77). The effects of pile irradiation on 1-decyne, 1-heptadecyne, 1-octadecyne, 9-octacosyne, 11-docosyne, and 16-dotriacontyne have also been reported (132). In all cases the predominant effect is the formation of condensed products from gaseous reactants, and of cross-linked products of higher molecular weight from liquid reactants, with little gas evolution.

At present only the work on acetylene merits a more detailed discussion. When gaseous acetylene is irradiated with  $\alpha$ - or  $\beta$ -particles,  $\gamma$ -rays, or slow electrons, the main product is a yellow solid which absorbs oxygen. About 15-20 per cent of the acetylene irradiated by  $\alpha$ -particles forms benzene (510),

whilst after irradiation with  $\gamma$ -rays an aromatic compound of molecular weight greater than that of benzene was detected (74). The overall decomposition yields of acetylene are  $-G_{\alpha}(\text{C}_2\text{H}_2) = 75$  and  $-G_{\beta}(\text{C}_2\text{H}_2) = 93$ .

The available evidence gives no satisfactory conclusion as to the mechanism of these processes. A free-radical or ionic chain mechanism might be expected (247, 389, 510), but neither these nor the original suggestion of a cluster mechanism (371, 372, 373, 462) has been established. Facts which are difficult to explain on the basis of a chain mechanism are the following: (a) the polymer yield is independent of the dose rate over appreciable changes of pressure, dose rate, and partial pressure of added inert gases; (b) the reaction is very reproducible and not easily inhibited; (c) change of temperature has little effect on the reaction, unlike the photochemical polymerization of acetylene (383); and (d) no equivalent yields of benzene have been detected in photochemical polymerizations (462).

On the other hand it has been claimed that a cluster mechanism cannot explain the yields of benzene (510), though formally this seems to present no difficulty. Current concepts do not favor cluster mechanisms, but no champion of a chain mechanism has yet succeeded in satisfying all the facts appropriate to this particular reaction.

It seems most likely that the mechanism of the reaction is primarily ionic, and possible reasons for this have been advanced (90). Recently some evidence of there being two concurrent mechanisms has been obtained (77), and it has been suggested that the reaction proceeds via *excited* acetylene molecules (620), but detailed interpretations are not available. Measurements of the molecular weights of the polymers might help in elucidation of the mechanism, but no solvent has yet been found.

## 2. Pure ethylenic hydrocarbons

The effect of the  $\alpha$ -particle irradiation of ethylene (371), propylene (285), isobutylene (456), 2-butene (284), cyclopentene (287), and cyclobutene (288) is to give liquid products, together with some gas. The yields of gas are less than for the corresponding saturated compounds and greater than for the corresponding acetylenic compounds, whilst the opposite is true of the overall yields (see table 1). The effects of electron bombardment of the following compounds have been examined: ethylene (427), octylene, diisobutylene, 1-methylcyclohexene, pinene (525), and cyclohexene (83, 412, 525), the results being qualitatively the same as in the investigations with  $\alpha$ -particles. Decene, and the *cis* and *trans* forms of the nine isomers of octadecene, have been irradiated in the pile (132). From this last investigation the *trans* isomer, rather surprisingly in view of the mass spectrometric results (page 479), was found to give higher yields of cross-linking than the *cis* isomer. The lower tendency to form cross-links exhibited by the octadecenes with the double bond farthest from the end of the chain and the relation of this result to mass spectrometric observations have already been mentioned.

Ethylene was the first compound of this class to be polymerized by ionizing

radiation (458), though it had been studied in electrical discharges very much earlier (256). In addition to the earlier studies with  $\alpha$ -particles and electrons, the effects of  $\gamma$ -rays have recently been investigated (74, 75, 76, 206, 283, 369, 542).

At 25°C. and pressures about atmospheric, the product of  $\alpha$ -particle irradiation is a colorless liquid of the empirical formula  $(\text{CH}_{1.7})_n$  (381). The overall decomposition yield is  $-G_\alpha(\text{C}_2\text{H}_4) = 18.1$ , and in the early stages the yield of hydrogen and methane together is about 16 per cent of this. At 0°C. and 31°C. the yields were found to be  $-G_\alpha(\text{C}_2\text{H}_4) = 18.5$  and 30.9, respectively (456). Under these conditions the mechanism evidently involves a considerable degree of condensation. Similar results were obtained from irradiation with electrons (427). The liquid product had a high viscosity and a low vapor pressure; it was soluble in chloroform but only partially soluble in alcohol, indicating the presence of more than one component. It decolorized bromine and potassium permanganate solution, and possessed an odor like that of higher unsaturated hydrocarbons. The gas evolved consisted mainly of hydrogen, methane, and ethane, with a small amount of acetylene. The kinetics of the reaction are not typical of a single chain mechanism.

On the other hand, all the results obtained from the irradiation of ethylene with  $\gamma$ -rays seem to indicate a chain mechanism, and the products differ in many respects from those obtained in the work with  $\alpha$ -particles and electrons. The reaction has been carried out under widely differing conditions of temperature and pressure, and the resulting products in the condensed phase differ markedly in appearance and properties, whilst in no case has any significant amount of gaseous product been reported. At room temperature and atmospheric pressure, and with dose rates of the order of 1000 r/min., the polymers are yellow or brownish solids and  $-G_\gamma(\text{C}_2\text{H}_4) = 107$  (75). Increasing the pressure to 21 atm. or above, whilst still at room temperature, produces a white waxy solid [ $G_\gamma(\text{polymer}) \sim 2500$  (283, 369)], whilst at about 100 atm. the polymer was formed in three layers, as a white solid, a spongy material, or a white curd, apparently depending on the dose rate at the particular point in the cell (206). Increase of temperature above room temperature at high pressure leads to polymers more liquid in nature and to even higher yields [ $G_\gamma(\text{polymer}) \sim 12,000$  at 21 atm. and 237°C. (206, 283)], unless the pressure is very high (2,000 atm.) and the dose rate low (542). Under these last conditions the polymerization tends to be complicated by a thermal reaction of rate comparable to that of the reaction initiated by  $\gamma$ -rays. The effect of oxygen on the polymerizations appears to be in some doubt. On the one hand strong inhibition by oxygen has been reported (283), whilst other workers find no effect upon adding small amounts of air, acetaldehyde, acetone, water, or carbon dioxide to the system (369). Though this throws doubt on the free-radical nature of the reaction, the large yields necessitate the assumption of a chain mechanism.

### 3. Dienes

As already noted, the presence of two double bonds in a chain renders the chain more prone to polymerization than one such bond alone. The yields of conversion

of allene and isoprene under irradiation with  $\alpha$ -particles (284) and of 2,5-dimethyl-1,5-hexadiene with pile irradiation (132) bear this out (see table 1). The high conversion yields of allene and isoprene, and also of vinylacetylene, under irradiation with  $\alpha$ -particles (286) may indicate that with these smaller molecules some addition-polymerization of the free-radical type does occur. Isoprene in particular exhibits a change in yield as the reaction proceeds, a result which would be in accord with a free-radical chain mechanism. On the other hand, the rate of the  $\gamma$ -ray-initiated polymerization of butadiene has been found to be only one-twentieth that of styrene under comparable conditions (110).

#### 4. Mixtures with other substances

Investigations of this kind have been restricted to ethylene and acetylene. In the presence of oxygen in equimolecular amount acetylene is oxidized by  $\alpha$ -particle irradiation to carbon dioxide and monoxide, little or no water being formed and the normal polymerization being completely inhibited. A clear colorless liquid of empirical formula  $(C_2H_3)_x$  is also produced (380). By contrast the addition of hydrogen does not prevent the polymerization of acetylene from being the main reaction under  $\alpha$ -particle irradiation, only a little hydrogenation resulting (380). Similarly the  $\alpha$ -particle irradiation of ethylene in admixture with hydrogen gives rise to practically no hydrogenation to ethane (371), the main reaction being polymerization of ethylene, with  $G_a(\text{polymer}) = 17.5$ .

The  $\alpha$ -particle irradiation of acetylene mixed with nitrogen, hydrogen, neon, argon, krypton, or xenon was found to give rates of polymerization proportional to the total ions produced from the acetylene and the inert gas together (378). This was formerly thought to imply that the polymerization was dependent on ionization only (374). However, recent work indicates that the ratio  $W/I = 1.71$  (where  $W$  = average energy expended in creating one ion pair and  $I$  = first ionization potential) for five of the inert gases and leaves open the possibility that excited states may contribute to the polymerization of acetylene, provided the part they play is in a constant ratio to the part played by ions (375). In view of the fact that all the gases have ionization potentials higher than that of acetylene ( $I_{C_2H_2} = 11.4$  e.v. (141)), the inert gases seem most likely to act by an indirect action mechanism, ionization (and possibly excitation) transfer occurring to the acetylene molecules. This is supported by the fact that the polymerization yield begins to fall at low enough concentrations of acetylene. An earlier objection to this view (371) was based on an incorrect value for  $I_{C_2H_2}$  of 12.3 e.v., a value which is greater than that of  $I_{Xe}$  (= 12.1 e.v.).

The behavior of mixtures of acetylene and carbon dioxide under  $\alpha$ -particle irradiation appears to be somewhat different in that the yield of polymerization is not maintained as the proportion of carbon dioxide is increased (378). It has been suggested that this is due to inefficient transfer of energy from carbon dioxide to acetylene, and this agrees with the finding that the carbon dioxide produced during the radiation oxidation of carbon monoxide or methane does not influence the progress of the reaction (371). In this connection it should be noted that although the ionization potential of carbon dioxide is higher than that

of acetylene, its electron affinity, unlike that of the other gases already mentioned, is also higher. Carbon dioxide and oxygen are thus similarly related to acetylene in this respect. The presence of oxygen leads only to oxidation, and carbon dioxide also seems to play a chemical part, since 10 per cent of the gas was not recoverable after the irradiation (371). On the other hand, the results have been interpreted in terms of a modified cluster theory (450, 451).

Mixtures of ethylene and acetylene have been irradiated with 1 m.e.v. electrons to give butadiene, but the exact conditions have not been quoted (204). Mixtures of ethylene and sulfur dioxide gave a copolymer of the two compounds when irradiated with  $\gamma$ -rays at room temperature and at very high pressures (369). The polymer was rather unstable.

The  $\gamma$ -ray irradiation of 1:1 mixtures of ethylene and oxygen in aqueous solution under a pressure of 120 lb./sq. in. gave acetaldehyde as the major product, with a high maximum yield of  $G_r(\text{CH}_3\text{CHO}) = 60$  (292). Ethanol and acetic acid were formed later and in lower yield.

### C. VINYL COMPOUNDS

Whether vinyl compounds are irradiated as pure compounds, or in solution, as solids, liquids, or gases, the most important effect is the initiation of their polymerization. The high energy yields which result indicate that the mechanism must be a chain, and all the evidence points to this being of the free-radical type. Thus the polymerizations can be inhibited by oxygen and benzoquinone, and the products generally possess properties typical of polymers produced by free-radical chain processes, such as high molecular weights. In the case of styrene and methyl methacrylate, direct evidence from copolymerization studies has shown conclusively that the radiation-induced polymerization of these two monomers proceeds by a radical mechanism (27, 31, 384) and that the propagating radical is a monoradical (544).

No linear energy transfer effects have been observed, but no direct comparative studies using radiations of widely different characteristics have yet been made. On the other hand, certain anomalous kinetic results have been attributed to the effect of a non-uniform distribution of the initiating entities arising from ionizing radiations (see below).

#### 1. *Mixtures with other substances*

The radiation-polymerization of vinyl monomers in mixtures is of interest from three points of view: it provides a method of obtaining information about the free radicals and molecular product formed from the solvent in the primary act; it is a convenient method of polymer preparation; and it may assist in the elucidation of the mechanism of the action of biological protection agents.

Vinyl monomers are generally efficient "radical scavengers." Consequently vinyl compounds in solution have been used to pick up radicals formed from the irradiation of solvents, and to make deductions concerning the nature and yields of the primary products arising from these solvents. Investigations of this kind include the polymerization of acrylonitrile in water (148, 162, 164, 220),

of styrene in a variety of solvents (110, 116, 356, 489, 545), of methyl methacrylate in a variety of solvents (110, 545), of acrylonitrile in methanol (110), and of acrylamide in water (149). An irradiated solution of monomer gives rise to a polymer, the end groups of which may be analyzed and so provide some indication of the possible radicals which initiated polymerization (148, 164, 220). The same initiation process serves to remove radicals which might otherwise destroy "molecular" products from the solvent, thus facilitating measurements of yields of the latter. But the scavenging power of a monomer may also be sufficiently high to remove the precursors of molecular products before these products have a chance to form. This is the case with acrylamide in aqueous solution which, when in sufficiently high concentration, reduces the yield of "molecular" hydrogen peroxide from water irradiated with x-rays (149). In determining the relative yields of primary products from different irradiated solvents, by measurement of the rate of polymerization of the same monomer in each solvent, two assumptions are made: (1) the mechanism of polymerization always involves a mutual termination of the growing chains; (2) the radicals are formed independently from monomer and solvent. The second assumption ignores the possibility of transfer of excitation or ionization between solvent and monomer before the formation of free radicals and may explain why abnormally high yields were found in certain cases (489). The assumption of mutual termination leads to an expectation of a rate of polymerization proportional to the monomer concentration and the (dose rate)<sup>1/2</sup>. Such a law appears to hold, except at high dose rates, for all the systems investigated in which the polymer formed is soluble in the solvent-monomer mixture, i.e., styrene in benzene, cyclohexane, ether, methanol (with more than 30 per cent styrene by weight) (109), or toluene (119, 121), and acrylamide in water (149, 540). On the other hand, in those cases in which the polymer formed is insoluble in the monomer-solvent mixture, quite different kinetic results have been obtained. In the case of acrylonitrile in water the rate of polymerization was found to depend on the square of the monomer concentration and on a power of the dose rate varying between 0.95 and 0.25, depending on the dose rate (148). An attempt was made to interpret these results on the basis of an increasing uniformity of initiating radical distribution with increasing dose rate, but they may be manifestations of the non-homogeneity of the system, for it has since been shown that a 30 per cent solution of acrylonitrile in dimethylformamide (in which mixture the polymer is soluble) gives a polymerization rate proportional to (dose rate)<sup>0.55</sup> (53). In mixtures containing a higher percentage of acrylonitrile (in which the polymer formed is insoluble) abnormal behavior results (487), similar to that shown by styrene in alcohols (109). It appears that only when a system is discovered which remains homogeneous when polymer is formed, and which also exhibits abnormal radiation-polymerization kinetics, can such studies be used to give unambiguous information regarding non-uniformity of radical production in the system. There is some indication of such behavior in the polymerization of solid acrylamide (see below). Identification of post-irradiation polymerization with inhomogeneity, which has been suggested (118), cannot easily be justified, for in two homogeneous systems,

methacrylic acid in water (231) and acrylamide in water (149), post-irradiation effects have been observed. The cause of these effects is not yet clear.

From a preparative point of view the initiation of polymerization with ionizing radiations, particularly with  $\gamma$ -rays, offers some unique advantages. It can be carried out at low temperatures, there is no danger of residual catalyst being left in the polymer, and, owing to the non-selective nature of the absorption of  $\gamma$ -ray energy, the rate of initiation can in principle be as low or as high as required, whilst yet being essentially uniform throughout the system, whatever the monomer concentration. This gives a useful control over the nature of the products. For example, the chain length of polyacrylonitrile can be varied over a very wide range by changing the dose rate and concentration (148). The same is true of polyvinylpyrrolidone; and an additional observation here, important from the point of view of the use of this polymer in blood plasma, is that the molecular weight distribution is appreciably narrower than that of polymers prepared catalytically (31).

Polymerization by irradiation of aqueous solutions has been used in an effort to determine the mechanism of action of biological protection agents. Many chemicals have been shown to be capable of protecting living organisms against the effects of ionizing radiations, but though a considerable amount of data is now available on the relative efficiency of different materials in this respect, there is still uncertainty concerning the mechanism of their operation. In some cases protective power runs parallel to the capacity to act as a chain-transfer agent in the polymerization of acrylonitrile (488), but this is not invariably true (25).

Preliminary work has been carried out on the emulsion-polymerization of styrene brought about by radiation (29). Higher rates and molecular weights than those for the same polymerization in bulk were found.

## 2. *Pure monomers in the liquid phase*

In principle there is no difference between the radiation-polymerization of pure monomers and of monomers dissolved in another material. There is merely initiation (and possibly termination) of polymerization by radicals formed from the monomer, instead of from the solvent and monomer together. Consequently the net rate depends both on the rate constants of the particular polymerization and the ease of breakdown of the monomer to initiating radicals. As for polymerization in solution, the rate of polymerization below certain dose rates has been found to be proportional to (dose rate)<sup>1/2</sup> for the two monomers studied which are capable of dissolving their own polymers: viz., styrene (26, 108, 109, 116, 119, 121) and methyl methacrylate (120). It has been suggested that at higher dose rates the rate of polymerization should become proportional to (dose rate)<sup>x</sup>, where  $x \rightarrow 0$ , the effect being in no way specific to radiation-polymerization but resulting from a change-over from mutual termination of growing chains to termination by initiating radicals, as these are formed in greater numbers (119). For styrene in toluene solution this concept is borne out (119), but for pure styrene it has been claimed that with dose rates below 1150 r/min.  $x = \frac{1}{2}$ , whilst above this dose rate  $x \rightarrow 1$  (26).



For those cases in which the polymer is insoluble in the monomer, the value of  $x$  tends to be greater than  $\frac{1}{2}$ . Thus acrylonitrile, which at first was reported to give  $x = \frac{1}{2}$  (486), was later found to give  $x = 0.68$  (55) and  $0.75$  (490). This was attributed to the existence of two types of termination (55) but seems more likely to be related to the inhomogeneity of the system. Vinyl chloride also gives  $x$  somewhat greater than  $\frac{1}{2}$  (118).

Less detailed investigations have been made of the effects of various radiations on styrene (30, 70, 307, 308, 486, 522, 544), methyl methacrylate (30, 110, 116, 308, 309, 486, 502, 522, 544), vinyl acetate (70, 110, 116, 307, 308, 309, 486), acrylonitrile (116, 486, 522), vinyl chloride (110, 453), and methyl acrylate (110, 522). In all the reports but one, polymerization resulted, and the products were not noticeably different from those obtained by non-radiation methods. It is interesting that no apparent polymerization was caused in vinyl acetate, styrene, propylene, or isobutylene by irradiation with electrons at very high dose rates but with very short exposures (70). This may have been due to the fact that at the high dose rates employed the chain lengths were so short that the products could not be regarded as high polymers. Similarly, it has been shown that with acrylonitrile at low concentrations in water an electron dose rate of about 10,000 r/sec. gives a high proportion of water-soluble "polymer" having an average chain length of only one to two units (147). The detailed investigation of the products of radiation-polymerization has not so far received much attention. In view of the variety of effects of radiation on polymers (see below), it seems possible that the products of radiation-induced polymerizations may be different from those of thermally or catalytically induced polymerizations, though in most cases the doses required for polymerization are much less than those required to produce appreciable changes in polymers. The  $\gamma$ -ray polymerization of perfluoropropylene, perfluorobutadiene, perfluoroacrylonitrile, perfluoroisobutylene, perfluoroamylpropylene, and 1,1-dihydroperfluorobutylacrylate (29) is unique, inasmuch as no other method for polymerizing these substances has yet been found. The first five monomers gave liquids or solids of very low chain length, whilst the last was converted to a rubbery polymer which was highly cross-linked. More useful polymers of the first monomers may conceivably be produced at high pressures.

Another result which appears to be specific to radiation initiation is the possibility of polymerization at very low temperatures or even in the solid state (see below). Tetraethylene glycol dimethacrylate has been polymerized at  $-55^{\circ}\text{C}$ . with 800 kv. electrons (522).

### 3. Polymerizations in the solid phase

Thermal polymerization of acrylamide does not occur below its melting point, but polymerization in the solid state is readily induced by  $\gamma$ -ray irradiation (29, 289, 434, 435). The speed of polymerization decreases as the temperature is decreased, and at low temperatures ( $-18^{\circ}\text{C}$ .) no appreciable polymerization occurs until the irradiated solid is warmed. Then, at a temperature of about  $22^{\circ}\text{C}$ ., the whole mass warms up considerably and polymerization occurs. Similar behavior was observed with tetraethylene glycol dimethacrylate (522), and

though it appears that the initiating radicals are in some way "frozen" in the solid, the true mechanism is by no means understood. During the polymerization the crystallinity of the system shows a marked decrease and disappears completely at 100 per cent polymerization (29). The rate of polymerization is proportional to the dose rate, and the molecular weight of the polymer is independent of the dose rate over the range 3000 to 900,000 r/hr. (26). This behavior would result if the polymerization were taking place in quite independent "volume elements" or "tracks" (*cf.* 148). At 35°C. the plots of yield versus dose are linear almost to 100 per cent polymerization (29), a result which indicates that the rate of initiation is constant or increasing. This would be expected if initiating radicals were produced from the polymer as easily as, or more easily than, from the monomer. The latter may well be the case in view of the fact that the presence of unsaturation tends to stabilize the monomer.

Interesting possibilities arise from the phenomenon of polymerization in the solid state. The order in a solid may give preference to a type of addition not normally encountered in the liquid phase, and it may be possible to polymerize monomers such as allylic compounds which otherwise do not polymerize at all or only with difficulty. The effect of  $\gamma$ -rays on solid solutions of two monomers, or of polymer and monomer, may provide useful methods of preparing graft and block copolymers in a controlled manner.

Other monomers which have been polymerized as solids are methacrylamide, methylene bisacrylamide, acrylic acid, methacrylic acid, *N*-vinylcarbazole, and *N*-vinylpyrrolidone (26).

#### 4. Polymerizations in the vapor phase

The study of the radiation-polymerization of vapors of vinyl compounds has been restricted to vinyl chloride irradiated with the  $\alpha$ -particles from radon mixed with the monomer (453, 454, 455, 460, 461). The rate of polymerization is proportional to the dose rate (460, 461), to the square of the pressure of monomer at low pressures (454, 461), and to the first power of the pressure at high pressures (454). Though the number of polymer chains initiated per  $\alpha$ -particle was the same in the vapor as in the liquid phase, the overall rate of polymerization was about 50 per cent greater in the liquid phase (453). Small amounts of added oxygen gas ( $\sim 0.3$  per cent) had little effect, for though the oxygen was used up in terminating chains it also formed a catalyst (461), presumably a peroxide.

### D. HALIDES

#### 1. The radiosensitivity of the halides

It has been known for some time that organic halides are highly radiosensitive. The evidence includes the ease of decomposition of cholesterol when dissolved in chloroform or carbon tetrachloride (see page 536), and recent studies using diphenylpicrylhydrazyl (DPPH) and polymerization methods for radical capture have confirmed that halides are among the most radiosensitive of compounds (489, 545).

The kinetics of the disappearance of DPPH present interesting features. It is found that with chloroform or carbon tetrachloride as solvent there is a pronounced after-effect (113, 115, 489), which is especially great for oxygen-free solutions (67). This is not due to a slow destruction of DPPH by products of irradiation such as chlorine or hydrochloric acid, because these substances react rapidly with DPPH (67). The explanation may rather be that some of the irradiation-produced free radicals are themselves too stable to react at once with DPPH. A useful approach to the understanding of the primary act in iodides has been to irradiate alkyl iodides in the presence of radioactive iodine. On irradiation in either the vapor or the liquid phase the added iodine exchanges with bound iodine, and consequently the carbon-iodine bond must have been broken by radiation (253). The results of irradiating alkyl halides may therefore be interpreted in terms of fission of the carbon-halogen bond, followed by further reactions of the highly reactive fragments. One of the reasons that this bond is broken may be that much of the weight of the molecule is concentrated in the halogen atom and a corresponding proportion of the energy is absorbed there. However, even if this were not so, it would still be possible for the carbon-halogen bonds to be broken preferentially; there are many examples in radiation chemistry of intramolecular transfer of energy from the point of absorption to the weakest bond.

## 2. Chlorides

Pure dry chloroform irradiated in the absence of oxygen gives hexachloroethane but practically no hydrochloric acid (539). Earlier investigators had reported that large quantities of hydrochloric acid were formed under these conditions, but little hexachloroethane (159, 265). The discrepancy may be due to impurities present in the samples used by the early workers, for the effect of impurities has been shown to be extremely marked.

The effect of oxygen on the reaction is striking, the chloroform being oxidized by a chain mechanism to give a peroxide as the primary product (539).



As the reaction proceeds the peroxide disappears, probably to give phosgene, and after long irradiation no peroxide remains. Phosgene is probably a primary product as well as a secondary product, because it is also formed at the beginning of the reaction, although in much smaller yield than the peroxide. Another primary product formed in small yield is chlorine. This does not build up but disappears by the thermal reaction (63, 271, 325):



Hexachloroethane is a product formed in relatively small yield (63, 325, 539). The production of hypochlorous acid has been reported (159, 265), but the analytical method seems to have been at fault (271). A complete material balance for the radiation-induced oxidation of chloroform cannot yet be given. The

system is a difficult one to work with because of the strong effect of impurities, characteristic of a chain reaction.

The radiation chemistry of methylene dichloride may resemble that of chloroform, for a peroxide is formed on irradiation in the presence of oxygen (539). Carbon tetrachloride and tetrachloroethylene, however, do not give a peroxide, possibly because hydrogen atoms are lacking, but both substances give phosgene and chlorine (265, 325, 539).

Halides have been irradiated in solution (in water and in organic solvents) and have been found to give acids (442, 443, 444). The yield is not always high enough to be proof that a chain reaction is occurring, but one halide which was irradiated, chloral hydrate, gave hydrochloric acid with a yield up to  $G_x(\text{HCl}) = 240$ , so that chain reactions are possible in aqueous solution as well in the pure state (18). The chloral hydrate system has been studied by the rotating sector technique; the mean lifetime of the free radical chain was found to be 0.1 sec. (235, 236). By the same method a lifetime of about 1 sec. was found for the chain carrier in the aerated chloroform-water system, irradiated with  $\text{Co}^{60}$   $\gamma$ -rays or 24 m.e.v. x-rays (312).

### 3. Bromides

Aliphatic bromides give hydrogen bromide and bromine on irradiation (433, 538). The effect of oxygen on these reactions has not been tested, so the mechanism remains in doubt. The addition of triphenylmethane to ethyl bromide before irradiation results in a ten times larger yield of bromide ion on hydrolysis after irradiation, probably because of its effectiveness in capturing bromine atoms which would otherwise undergo back-reactions. Aliphatic bromides give hydrogen bromide on irradiation in aqueous solution.

### 4. Iodides

The radiolysis of the alkyl iodides is of particular interest, in that a comparison can be made with their photolysis. The two processes are found to be superficially similar. In both cases there is preferential fission of the carbon-iodine bond, for with labelled iodine present the principal reaction is exchange. The kinetics of the production of iodine from pure alkyl iodides are also similar, in that the iodine yield is proportional to the dose in both cases (366, 538, 584). Nevertheless, there are fundamental differences between the two processes, which are especially well established for methyl iodide (473, 538). The most important difference is that whereas the principal products of the photolysis of methyl iodide are methane and methylene iodide, with less iodine and ethane, radiolysis gives mainly iodine and ethane, with less methane and much less methylene iodide. It is also significant that the energy required for decomposition by ultraviolet light of wavelength 2537 Å. is about ten times that for decomposition by ionizing radiations. The difference between the photolytic and radiolytic processes points to a fundamental difference in mechanism, and it seems likely that ionic processes may play an important part in the radiolysis, although the free-radical processes occurring in the photolysis probably also occur.

The work on methyl iodide was with liquid samples in the absence of oxygen. In contrast to the findings for alkyl chlorides, oxygen has been reported not to exert a strong effect on the yield of iodine from the iodides (538). However, work demonstrating pronounced oxygen effects in such systems has been mentioned at meetings but has not yet been published.

Attempts have been made to compare the yield of iodine from the lower alkyl iodides (584). It appears that the yields of iodine from the radiolysis of the lower alkyl iodides increase regularly as the fraction of the hydrogen atoms in the molecule which are on the carbon atom in the  $\beta$ -position relative to the iodine bond increases (142).

The production of iodine from methyl- $C^{14}$  iodide by the action of its own  $\beta$ -particles constitutes a practical problem (612), and it has been suggested that storage in a suitable solution, instead of in the pure state, might decrease the extent of decomposition. Care would, of course, have to be taken in choosing the solvent, or the effect could be magnified.

### 5. Dosimetry

Several halide systems have been examined as possible chemical dosimeters for ionizing radiations. The first system suggested, a solution of iodoform in air-saturated chloroform (269, 270), was proposed as a dosimeter in 1904 (237) and has the advantages that the iodine liberated can be measured easily, and that the yield is high, enabling low doses to be measured. However, a study of the mechanism of the reaction revealed that the disadvantages are too great to permit its application to dosimetry (46, 265). In particular, the iodine is not liberated by an immediate effect of the radiation but is derived from the peroxide and other products formed from the chloroform. Consequently, the liberation of iodine is highly sensitive to impurities and is a slow process. The decolorization of diphenylpicrylhydrazyl in chloroform solution has also been proposed for dosimetry (112), but the slow continuation of reaction after the irradiation has stopped, although not quantitatively as important, would prove a disadvantage (115).

Pure alkyl iodides offer better possibilities. In this case the reaction is simpler, and the essential requirement, that of iodine liberation being proportional to dose, is fulfilled (366, 584). The iodide can be irradiated in ethereal solution instead of in the pure state if a dosimeter with the same electron density as water is required for biological or other purposes. This technic may be suitable for electron irradiation or irradiation with  $\gamma$ -rays of such energy that the photoelectric contribution to absorption is negligible but would not serve for cases where photoelectric absorption is important, since the absorption coefficient is strongly dependent on atomic number.

The alkyl iodide dosimeter, though probably quite a good one, does not appear to possess any advantage over the widely used, and exhaustively studied, aqueous ferrous sulfate dosimeter (see 197, 438). For some purposes (e.g., civil defense) it is desirable to have a more sensitive system, and halides have special advantages in this direction. In particular, use can be made of the chain reactions which occur, although this necessarily entails a sacrifice of reproducibility. On

irradiating chloroform-water mixtures, the peroxide and other products formed by a chain reaction all give hydrochloric acid, and so by using a suitable pH indicator a very sensitive system can be obtained, suitable for doses as low as 10–100 r (599, 600). It is also possible to use the production of oxidizing entities directly, as is done in the bromoform-leucocrystal violet dosimeter, in which the leucocrystal violet is oxidized to a carbinol base; this system is one of the most sensitive yet discovered (585). It may be concluded that the use of halides in dosimetry may turn out to be of particular importance in the field of low doses.

#### E. ALCOHOLS, HYDROXY ACIDS, AND CARBOHYDRATES

The effect of ionizing radiations on alcohols and related compounds fits into the general pattern of fission of one of the alpha carbon-hydrogen bonds to give hydrogen and a radical, which can either give a dimer ( $\alpha$ -glycol) or be further oxidized to give a carbonyl compound. This pattern applies whatever the phase and, in the liquid phase, whatever the solvent.

##### 1. Alcohols

The results on methanol provide a good illustration of the above generalization. When pure liquid methanol is irradiated with  $\alpha$ -particles, hydrogen is evolved and formaldehyde and ethylene glycol appear. Minor products are also present, but these three are formed in greatest yield (425). Linear energy transfer effects are apparent, for when methanol is irradiated with  $\gamma$ -rays it gives mainly hydrogen and ethylene glycol, with much less formaldehyde than from  $\alpha$ -particle irradiations (424). Similarly, when methanol- $C^{14}$  is decomposed under the influence of its own  $\beta$ -particles it gives hydrogen and ethylene glycol, but no formaldehyde (556).

The effect of  $\alpha$ -particles on pure liquid alcohols has been studied intensively (425). Hydrogen is the principal gaseous product from all the primary and secondary alcohols irradiated (72, 425). Only one tertiary alcohol (*tert*-butyl alcohol) has been irradiated, and this gave more methane than hydrogen. The reason may be that no alpha carbon-hydrogen bonds are present, and the next most readily broken bonds, the alpha carbon-carbon bonds, are broken instead. Examination of the nature of the small amounts of hydrocarbons produced from straight-chain alcohols confirms that the alpha carbon-carbon bonds are not difficult to break, for the hydrocarbons consist principally of those with one less carbon atom than the original alcohol. A similar explanation applies to the production of hydrocarbons from branched-chain alcohols.

Dehydrogenation is believed to give an  $\alpha$ -hydroxyalkyl rather than an alkoxyl radical, for  $\alpha$ -glycols are formed rather than peroxides. There does not seem to be any simple relationship between the yields of carbonyl compounds and glycols, although both are formed in very roughly the same yield, except for the tertiary alcohol which gave only a carbonyl compound. The carbonyl compounds from primary alcohols are predominantly the corresponding aldehydes. Secondary alcohols give both ketone and aldehyde, and the tertiary alcohol gives only ketone.

Alcohols with very long chains appear to give less aldehyde and glycol than alcohols with shorter chains, presumably because the influence of the hydroxyl group is lessened at a distance and the alcohol begins to behave like a hydrocarbon. However, in view of the apparently anomalous behavior of carboxylic acids with increasing chain length (page 495), this point should be checked by the irradiation of a wider range of alcohols.

Water is always formed during the radiolysis of alcohols, in about the same small yield for each, but at present no explanation for this can be given (322, 425).

On prolonged irradiation the primary products of the irradiation of alcohols are themselves affected. Thus, in the vapor phase the aldehydes formed by the action of electrons give polymers which in turn are attacked to give gaseous products (428).

When pure liquid alcohols are irradiated in the presence of oxygen, aldehydes, carboxylic acids, and per acids appear (322, 332). It is not certain whether the acids are primary products or not, although it is known that in the absence of oxygen acids are not formed as primary products (425).

Aqueous solutions of alcohols give hydrogen, aldehydes, glycols, and acids on irradiation (242, 333, 401, 423, 526, 589), but it is again not certain whether the acids can be regarded as primary products or whether they are derived from the aldehydes. The yield of hydrogen from aqueous alcohols is greater than can be accounted for by the action of radiation on the water alone (e.g., from ethanol  $G_2(\text{H}_2) = 2.8$  (591)), so that besides the expected oxidation of alcohols by hydroxyl radicals there may also be some dehydrogenation by hydrogen atoms.

The yield of acetaldehyde from aqueous ethanol increases when dissolved oxygen is present (589), and organic peroxides also appear, again possibly as secondary products (401).

## 2. Hydroxy acids

Pure hydroxy acids have not been irradiated, but  $\text{C}^{14}$ -labelled calcium glycolate is known to be decomposed, with a rather large yield, under the influence of its own  $\beta$ -particles (367, 607, 608); the products are formic and oxalic acids (609).

When aqueous solutions of hydroxy acids are irradiated, keto acids are formed. For example, lactic acid gives pyruvic acid (192), and malic, citric, and  $\beta$ -hydroxybutyric acids all give the corresponding keto acid (485). As is usual in aqueous solutions, the oxidation yield is greater with oxygen present (317, 485).

## 3. Carbohydrates

The results of irradiating polyhydric compounds in aqueous solution are interesting in that the secondary alcohol groups are found to be unaffected, whilst the primary alcohol groups are oxidized to aldehyde (474). The irradiation of aqueous D-manitol provides an example, for D-mannose is formed. On the other hand inositol, possessing only secondary alcohol groups, gives rhodizonic acid (541). On long irradiation the D-mannose produced from mannitol is oxidized to D-mannuronic acid. However this does not occur until quite high concentrations of D-mannose acid are built up, and radiation may therefore provide a useful

tool for preparing an aldose from the corresponding sugar alcohol. When aqueous hexoses are irradiated, good yields of the corresponding uronic acid are obtained, probably because the primary alcohol group is oxidized to give an unstable dialdose which changes to the hexuronic acid. For carbohydrates, as for alcohols and hydroxy acids, the presence of oxygen during the irradiation increases the yield of oxidized products.

The formation of acids when aqueous carbohydrates are irradiated (see also 157, 348) explains why sucrose is inverted when irradiated in aqueous solution (138, 139, 321, 501). In agreement with this explanation it is found that glucose is not inverted on irradiation in aqueous solution (322).

There are indications that glucose gives other substances as well as glucuronic acid on irradiation, but little is known of their nature (303, 557). The products of the irradiation of aqueous ribose have been determined, but very large doses were employed and only breakdown products were detected (532).

#### F. ALDEHYDES AND KETONES

In the vapor phase the electron irradiation of formaldehyde gives a polymer which is then further decomposed by radiation to give hydrogen, methane, carbon monoxide, and carbon dioxide. Acetaldehyde and acetone behave similarly, but the polymer appears as a yellowish solution in the original material (427).

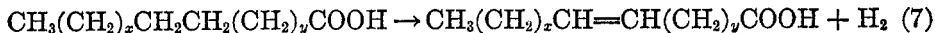
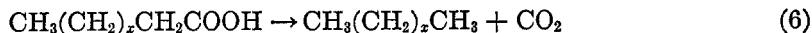
In the liquid phase propionaldehyde gives little solid product but is apparently decomposed directly into a mixture of gases. When hexadeuterobenzene is present, the decomposition is increased, probably because the lowest excited state of propionaldehyde is lower than that of hexadeuterobenzene and energy adsorbed by the benzene can therefore be transferred to the aldehyde (469) (see also aromatic compounds, page 502). Acetone gives an acid on prolonged irradiation (323).

In aqueous solution formaldehyde, acetaldehyde, and propionaldehyde give hydrogen, the corresponding acid, and probably other products. Acetone gives hydrogen but no acid (242). On prolonged irradiation with oxygen present, the acids give per acids (401, 402).

#### G. CARBOXYLIC ACIDS AND THEIR ESTERS

##### 1. *Pure acids and esters*

Two reactions are important in the radiation chemistry of pure carboxylic acids (624): one is decarboxylation to give a hydrocarbon; the other is dehydrogenation to give an unsaturated acid.



The decarboxylation has been well established by the identification of both hydrocarbons and carbon dioxide (305, 551, 626). Carbon monoxide and water are also produced in low yield, and from the fact that the ratio (hydrocarbon)/(CO<sub>2</sub> + CO + H<sub>2</sub>O) is constant for acids having a chain length of two to thirty



carbon atoms, it has been concluded that all these products arise in the same reaction.

The second reaction is not so well established, but hydrogen is invariably present (305, 551, 624), and polymerized products are not produced (92). It is therefore difficult to see what substances other than unsaturated acids could be formed by dehydrogenation.

Decarboxylation and dehydrogenation occur simultaneously but not apparently on the same molecules, as is indicated by the small amount of unsaturated hydrocarbons among the products (551). The effect of chain length on the efficiency of the two processes is not a simple one. The amount of decarboxylation decreases down to  $C_{22}$  and rises again at  $C_{30}$ . Dehydrogenation reaches a maximum at  $C_{16}$  and a minimum near  $C_{24}$  (624).

An important reason for studying the radiation chemistry of carboxylic acids springs from the idea that petroleum has its origin in the action of radiation on organic acids (552). This is a development of an older suggestion that petroleum is produced by the action of radiation on other hydrocarbons (379, 605). The greatest natural source of energy available for such reactions is  $\alpha$ -particles, and consequently most of the work with carboxylic acids has been with these.

A major objection to the hypothesis is that organic acids give hydrogen on irradiation, yet this is not found in oilfields (552). A possible explanation might be that under the influence of radiation the hydrogen hydrogenates unsaturated compounds. This reaction has been shown to occur on irradiation of oleic acid with  $\alpha$ -particles or deuterons, some stearic acid being formed (72, 92). Other products formed in this irradiation are polymerized acids, as expected from the presence of the double bond, and the decarboxylation product 8-heptadecene. The formation of the latter is of particular interest as it can easily be separated in a pure form, and indeed the action of radiation on oleic acid may be one of the best methods of preparing it (93).

Among other acids which have been irradiated is cyclohexanecarboxylic acid (73), which is both decarboxylated and dehydrogenated to give cyclohexane and cyclohexene. Some dicyclohexyl ketone has also been detected. Caproic acid gives some diamyl ketone as a minor product (72).

It is found that the percentage of hydrogen in the gas from irradiated salts and esters is greater than from the acids themselves (72). When dissolved oxygen is present, methyl stearate, methyl oleate, and methyl linoleate give a peroxide when irradiated with  $\gamma$ -rays. The amount of peroxide decreases slowly after irradiation (268).

## 2. Aqueous solutions

### (a) Formic acid

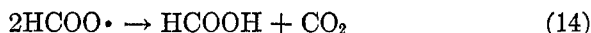
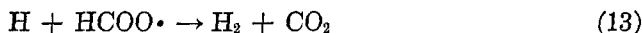
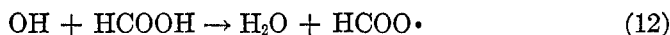
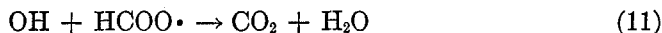
Formic acid is oxidized to carbon dioxide when irradiated in aqueous solution (329). Among the minor products are tartronic acid, oxalic acid, and formaldehyde (144, 250, 252). The formation of oxalic acid may be important when dilute solutions of formic acid are irradiated in the absence of oxygen above pH 3 (241, 242), but oxalic acid is not considered to be an important product under

other conditions. In air-free solutions  $\alpha$ -particles give more tartronic acid ( $\text{COOHCHOHCOOH}$ ) than oxalic acid (144, 250). Formaldehyde is normally formed only in small yield. Some of the kinetic results could imply that performic acid might be a product, but this has been shown not to be the case (278).

The kinetics of the  $\gamma$ -ray-induced oxidation of formic acid under various conditions have received careful study. In oxygen-free acid solutions, carbon dioxide and hydrogen are produced in equal amounts, and the yield is found to be independent of the formic acid concentration in the range 0.001–0.01  $M$ . These facts have been explained by the equation (276, 277)

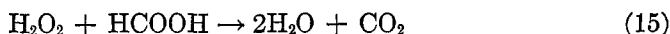


followed by either equations 10 and 11, or equations 12 and 13, or equations 10, 12, and 14, giving the net reaction 9.



It has so far not been possible to distinguish between the three paths. From experiments with  $\text{DCOOH}$  the intermediate radical is believed to be  $\text{HCOO}\cdot$  rather than  $\text{COOH}\cdot$ , the hydrogen produced from this substance consisting largely of  $\text{HD}$  (277).

When small amounts of hydrogen peroxide are present, the decomposition of formic acid proceeds with a rather large yield, up to 55 times as great as in the absence of hydrogen peroxide (276). Hydrogen is no longer a major product and the overall reaction is now:



The rate of carbon dioxide development increases at first with increasing hydrogen peroxide concentration, but after  $[\text{H}_2\text{O}_2] = 7.4 \times 10^{-4} M$ , it decreases again. Oxygen inhibits the reaction. The facts imply a chain reaction and can be explained by a mechanism comprising reactions 8, 10, 12, and 16.



At low hydrogen peroxide concentrations, the chain is terminated by some unknown entity,  $X$ .



At high hydrogen peroxide concentrations, the chain-termination reaction is:



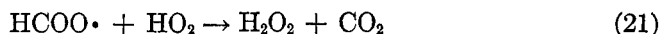
The inhibiting effect of oxygen on the above reaction is attributed to the removal of hydrogen atoms and  $\text{HCOO}\cdot$  radicals by reactions 1 and 19.



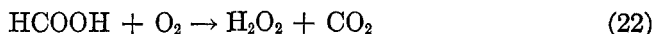
followed by either



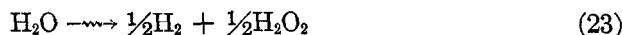
or



giving as the net reaction in the presence of oxygen:



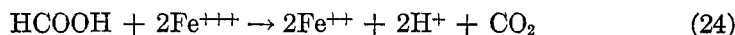
However, there is still a small amount of hydrogen formed from the primary step:



and the formic acid-oxygen system has been used to determine the yields of the primary reactions 8 and 23 (277, 280), giving results in good agreement with those from other systems.

At high concentrations (1 *M*) of formic acid a new effect seems to be present. This is the capture of recoil electrons by formic acid molecules, possibly to give formaldehyde (279). In strongly acid solutions ( $\text{pH} < 3$ ) the formic acid-oxygen system behaves slightly differently. More oxygen is consumed, more hydrogen peroxide is formed, and there is less carbon dioxide and hydrogen. These effects may be due to small changes in the mode of the radiation-decomposition of water in acid solutions (278).

Other radiation-induced reactions of formic acid include reaction with ferric ions,



a chain reaction with ferrous ions and oxygen (281),



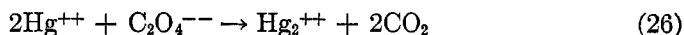
and also a reaction with ceric ions to give carbon dioxide, hydrogen, and oxygen (563).

#### (b) Other acids

It is a general observation that hydrogen always appears when air-free aqueous solutions of acids, or many other substances, are irradiated with x-rays (242, 507), but it is possible that this may sometimes be derived entirely from the water. Aqueous acetic acid has been shown to give succinic acid and hydrogen as important products (242, 249, 251), whilst hydrogen peroxide and carbon dioxide can also appear, depending on the conditions. With large doses tri-carballylic acid appears, and this is due to a further reaction on the succinic

acid (249). In concentrated solutions of acetic acid the direct effect of radiation begins to be significant, and carbon dioxide, methane, ethane, and carbon monoxide become important products (248).

Oxalic acid gives formic acid and carbon dioxide (242, 330, 472), together with hydrogen. The yield for the destruction of oxalic acid in air-saturated aqueous solutions is about the same whether neutrons [ $-G_n((\text{COOH})_2) = 5.2$ ] or  $\gamma$ -rays [ $-G_\gamma((\text{COOH})_2) = 4.9$ ] are used (198). An aqueous mixture of potassium or ammonium oxalate and mercuric chloride (Eder's solution) reacts by a chain mechanism when irradiated with x-rays,  $\gamma$ -rays, or ultraviolet light.



It is possible to use the weight of mercurous chloride formed as a measure of dose, but the method gives rather irreproducible results, like most chain reactions (139, 282, 632, 634).

Peroxy acids are formed when some acids, including crotonic, succinic, and fumaric acids, are irradiated in aqueous solution with oxygen present (401, 402). Peroxide formation is also an important part of the radiation-induced autoxidation of methyl linoleate emulsions, which has been studied for its biological importance (482). Various antioxidants can inhibit the autoxidation, lipid-soluble ones being especially effective. An emulsion of the methyl ester of  $\beta$ -eleostearate is also autoxidized (430). The simpler system, aqueous linoleic acid, has been shown to be oxidized in a chain mechanism, with oxygen present (429), and peroxide formation is presumably important here too.

Maleic acid, as might be expected from its unsaturated double bond, is polymerized when irradiated with  $\beta$ -particles in aqueous or ethereal solution (404). Isomerization to fumaric acid also occurs, and the radiation from radium gives the same maleic-fumaric equilibrium as is reached with ultraviolet light (324, 329).

## H. NITROGEN-CONTAINING COMPOUNDS

### 1. Quaternary ammonium compounds

The decomposition of pure choline methyl- $\text{C}^{14}$ -chloride by its own  $\beta$ -particle irradiation proceeds with a very high yield, probably owing to a chain reaction (367, 608), but other quaternary ammonium compounds are not as sensitive to radiation (368). 2-Chloroethyltrimethylammonium chloride, which is known to be thermally unstable, is not especially radiosensitive. Acetylcholine has been irradiated with x-rays in aqueous solution. It shows typical dilution and protective effects, indicating that the radiation acts indirectly (168).

### 2. Other compounds

Nitrogen mustards give hydrochloric acid on irradiation in aqueous solution (263). Piperidine on prolonged irradiation gives, amongst other products, an aldehyde, probably identical with  $\delta$ -aminovaleraldehyde. The aldehyde itself is further altered, to give condensation products (334).

## III. AROMATIC COMPOUNDS

The introduction of an aromatic ring into an aliphatic compound increases the stability of the compound towards ionizing radiations; other groups also tend to make the resultant reaction of the compound more specific, i.e., less in accord with the statistical hypothesis. On the evidence so far available, these effects seem most likely to arise from a stabilization of the primary products of irradiation, rather than stabilization of the molecule towards the attack of radicals formed in the primary act.

## A. HYDROCARBONS

As in the case of unsaturated aliphatic hydrocarbons, the predominant effect of the irradiation of aromatic hydrocarbons is the production of polymers. Table 2 illustrates the fact that although aromatic compounds are more radiation-resistant than their aliphatic counterparts, a completely false idea of the difference in stability may be obtained if only decomposition yields to gases are taken into account.

Very little information is available on the effects of linear energy transfer in aromatic hydrocarbon systems, and only one investigation has been deliberately aimed at a comparison of the effects of different radiations on pure hydrocarbons. It was found that pile irradiation of toluene, ethylbenzene, isopropylbenzene, and *tert*-butylbenzene gave higher yields of hydrogen and C<sub>2</sub> hydrocarbons, and lower yields of methane, than electron irradiation (596). However, it was not possible to suggest any definite correlation between the difference in behavior of the two types of radiation and their different values of linear energy transfer. Irradiation of isopropylbenzene with  $\alpha$ -particles also yielded appreciably higher amounts of hydrogen than irradiation with electrons (463). On the other hand, the same change in viscosity of toluene was observed, for a given input of energy, with either pile or  $\gamma$ -ray irradiation (102), indicating that the yields of polymer production in each case were not very different. There are differences in the results obtained with dilute aqueous solutions of aromatic hydrocarbons when irradiated with different radiations (see below), but these are really manifestations of the behavior of water.

TABLE 2  
*Comparison of the results of irradiating various classes of hydrocarbons*

	Vapor*			Liquid		
	<i>G</i> (polymer)	<i>G</i> (gas)	<i>G</i> (total)	<i>G</i> (polymer)	<i>G</i> (gas)	<i>G</i> (total)
Cyclohexene.....	10.5	5.8	16.3	12.4	1.4	13.8†
Cyclohexane.....	3.0	6.0	9.0	1.7	6.0	7.7†
Hexane.....	0.5	7.7	8.2	(1.7)§	4.4‡	6.1
Benzene.....	4.1	0.76	4.9	0.75	0.055	0.8¶

\*  $\alpha$ -Particles (295).

† 1.5 m.e.v. electrons (412).

‡ 0.17 m.e.v. electrons (calculated in reference 609 from results in reference 525).

§ For fast electrons and heptane (83); hexane would not be expected to behave very differently.

¶ 1.5 m.e.v. electrons (468).

## 1. Mixtures with similar hydrocarbons and with other substances

## (a) Free-radical yields

The polymerization method and the method using diphenylpicrylhydrazyl (DPPH) have both been used to obtain information on the yields of free radicals obtainable from aromatic hydrocarbons subjected to ionizing radiations. However, the investigations have not as yet yielded much information on the nature of these reactive entities. The earliest work with the polymerization method gave the following order of increasing radical yields for six hydrocarbons: benzene, styrene, toluene, *m*-xylene, ethylbenzene, and diphenylmethane (110), a result in conformity with evidence obtained from the irradiation of pure substances (see below). The DPPH method has been employed in the case of benzene and toluene only, giving results in qualitative agreement with those from the polymerization method. On the other hand the exact values of the radical yields deduced from the two methods remain in some doubt (see table 3). The only information regarding the nature of the reacting entity obtained by these methods is the observation that after the electron irradiation of DPPH in benzene, the composition of the principal fraction from chromatographic analysis suggested the addition of a  $C_6H_4$  fragment (625).

## (b) Hydrocarbon mixtures

The study of aromatic hydrocarbons in mixtures covering a wide range of composition has yielded useful information on the mechanism of decomposition and the processes of energy interchange between the components of such mixtures. The first such investigation—the x-ray irradiation of anthracene in phenetole or xylene or of dianthracene in xylene—was quite uninformative, producing no apparent change (139). A year later it was reported that the bombardment of a mixture of benzene and cyclohexane with 170 kv. electrons gave less total de-

TABLE 3  
Primary radical yields per 100 e.v. ( $G^R$ ) from aromatic hydrocarbons

Benzene		Styrene	Toluene	<i>m</i> -Xylene	Ethylbenzene	Diphenylmethane	Method	Radiation	References
Aerated	Air-free	Air-free							
—	1.2	1.2	1.79	5.18	7.5	—	Polymerization	$\gamma$	(108)
—	—	—	—	—	—	(57)*	Polymerization	$\gamma$	(110)
—	1.47	1.31	2.54	5.16	7.38	—	Polymerization	$\gamma$	(408, 489)
—	—	0.56	—	—	—	—	Polymerization	$\gamma$	(413)
—	1.04	—	1.83	—	—	—	DPPH†	$\gamma$	(111)
—	1.47	—	2.78	—	—	—	DPPH†	$\gamma$	(408, 489)
0.75-1.2	0.96	—	—	—	—	—	DPPH†	$\gamma$	(67)
0.6-0.7	0.8	—	—	—	—	—	DPPH†	$\epsilon$	(625)
—	>0.4	—	—	—	—	—	Pure substance	$\epsilon$	(87)
—	0.76	—	0.4	—	—	—	Polymerization (styrene)	$\beta$	(545)
—	0.34	—	—	—	—	—	Polymerization (methyl methacrylate)	$\beta$	(545)

\* Calculated by comparison with styrene and assuming a value of  $G^R = 1.3$  for this.

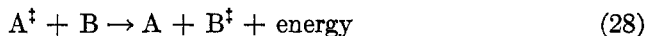
† Diphenylpicrylhydrazyl.

composition (as measured by gas evolution) than would be expected from the effects on the separate constituents (525). Not until much later was particular attention drawn to this result (82), and it was suggested that in view of the known susceptibility of benzene vapor to destructive decomposition by hydrogen atoms, it was unlikely that the effect was due to the removal of reactive intermediates in secondary reactions (83). As the formation of polymers is the most important reaction occurring in irradiated benzene (see below), and as no measurements of polymer yield were available for the benzene-cyclohexane system, the possibility remained that the polymerization reaction was accounting for radicals from the cyclohexane which might otherwise form gaseous products. But further work on the irradiation of the liquid systems toluene-benzene, cyclohexene-benzene, cyclohexane-benzene, and cyclohexane-cyclohexene with 1.5 m.e.v. electrons was satisfactorily explained on the basis of the occurrence of excitation and positive charge transfer between the components (412).

If in a mixture of components A and B,  $I_A > I_B$  (where  $I$  = the lowest ionization potential), then positive charge may be transferred with high probability from A to B (411).



Excitation energy may behave similarly if  $E_A > E_B$  ( $E$  = the lowest excitation potential),



but the conditions necessary for a high probability of such an occurrence are rather more restricted. Moreover, if  $I_A > I_B$  it does not necessarily follow that  $E_A > E_B$ . The ionization potentials of the above compounds are as follows: toluene, 8.8 e.v.; cyclohexene, 9.2 e.v.; benzene, 9.4 e.v.; cyclohexane, 11.0 e.v. By considering the variation of the yields of the different gaseous products with varying composition of the mixture, it was shown that the results were consistent with the occurrence of charge and excitation transfer from benzene to toluene, and from cyclohexane to benzene, whilst in the case of benzene-cyclohexene mixtures it appeared that energy transfer occurred from cyclohexene to benzene (412). As a consequence of this the decomposition products from benzene-toluene mixtures arise largely from the toluene, which is said to offer "sacrificial" protection to the benzene (89). With cyclohexane-benzene mixtures the situation is rather different. Here the transfer of ionization and excitation energy from cyclohexane to benzene decreases the gas yield from the former without appreciably decomposing the latter, owing to the capacity of the aromatic system to delocalize energy and subsequently degrade it without chemical change. This has been termed "sponge-type" protection (89). In cyclohexene-benzene mixtures the benzene provides sponge-type protection by transfer of excitation energy from cyclohexene to benzene, and cyclohexene provides sacrificial protection by transfer of ionization energy from benzene to cyclohexene.

Despite the consistency of the above results with the postulated relevance of charge and excitation transfer, the validity of the concept was not substantiated

until the hexadeuterobenzene-cyclohexane system had been investigated (91). In these experiments, measurements of the electron irradiation yields of  $D_2$ , HD, and  $H_2$  with different concentrations of the components, coupled with a knowledge of the relative rates of the reactions



from other data (469), allowed a calculation of the maximum possible yield of  $H_2$  or HD at each concentration to be made. This was lower than the statistical expectation, fully confirming sponge-type protection by the benzene. In addition, the yields of HD and  $H_2$  gave an indication that a molecular decomposition of the type



became increasingly important at high concentrations of deuterobenzene. It was suggested that such a situation might arise by transfer of energy from a persistent triplet state of  $C_6D_6$  (energy 3.6 e.v.) to a triplet state of cyclohexane capable only of breakdown by a molecular process of the above type.

The above discussion refers to the liquid phase. In the vapor phase there is still some protection of cyclohexane by benzene, but the increased possibility of free-radical processes tends to make the situation less clear-cut (412).

With liquid mixtures of benzene and deuterobenzene, the yields of acetylene from electron bombardment are consistent with there being mutual protection so far as production of acetylene is concerned. The yields of hydrogen not only give a clear indication of the protection of benzene by the deuterobenzene, but also indicate that two simultaneous mechanisms occur, one via free atoms and the other via molecules formed in the primary act (262) (see also page 510). It is considered that a mixture of two highly resonant substances with slightly staggered energy levels, such as the benzene-deuterobenzene system, probably provides the best opportunity for energy transfer, and dissipation, without reaction.

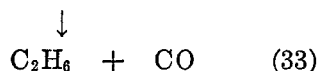
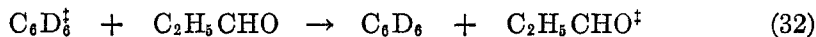
In view of the importance of polymerization in the radiation chemistry of aromatic hydrocarbons, it is unfortunate that in none of the above investigations has the polymerization reaction been followed directly.

### (c) Mixtures with other organic compounds

In the electron irradiation of mixtures of hexadeuterobenzene and propionaldehyde the linear dependence of the yields of methane and ethylene on the electron fraction of propionaldehyde, and the fact that an assumed linear dependence of the hydrogen atom yield leads to consistent results, indicates that the benzene exerts no protective effect on propionaldehyde. This suggests that propionaldehyde has an excitation potential lower than the known triplet state of benzene at  $\sim 3.6$  e.v. (91). In agreement with this notion the yield of ethane is greater than the statistical expectation, indicating a sensitization of the pro-



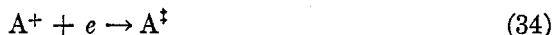
pionaldehyde decomposition by benzene. The different behavior of the yields of ethane, and methane or ethylene, implies that the decomposition to ethane does not involve free radicals, and it was suggested that the effective processes are



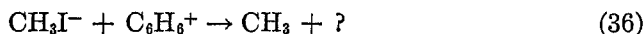
The excited propionaldehyde has insufficient energy to give radicals but is capable of yielding ethane by a molecular process involving lower activation energy. Sensitization and protection effects are also evident in the results from the irradiation of mixtures of benzene with chloroform or methyl acetate, the radical yield being obtained by the use of diphenylpicrylhydrazyl (DPPH) (67). It seems clear from this work that benzene in low concentration protects chloroform. The remaining examples are all of sensitization, but they cannot be fully interpreted from the data, particularly in view of the possibility of energy transfer to the DPPH.

#### (d) The mechanism of intermolecular energy transfer

In the previous sections two types of intermolecular energy transfer have been mentioned: viz., charge transfer and excitation transfer. The former must of course involve transfer of an electron, and this may occur either by a resonance process between two molecules of the same kind or by a non-resonant process between two molecules of a different kind, with or without chemical decomposition. Some aspects of such processes have been discussed (90, 411); complex formation is involved, and two potential curves of the complex must cross. Recently it has been suggested (469) that only excitation transfer is relevant to radiation chemistry, back-reactions of the type



occurring in a time less than  $10^{-13}$  sec. (520). This hypothesis, however, has met with some opposition (480), and experiments have indicated that processes of electron capture, probably of the following type, may play a major part in the decomposition of alkyl halides or acetic acid in hydrocarbon solutions (628).



The mechanism of excitation transfer is still in some dispute. To date the most informative studies on this subject have been those concerned with scintillations produced from solid or liquid mixtures of suitable organic compounds under the action of ionizing radiations. In such cases it has been shown that energy absorbed by a major component may be transported with high efficiency to a minor component over distances of the order of 50 Å. or more, before finally being liberated as the fluorescence radiation of the minor component (1, 68, 143, 245, 335, 336, 353, 354, 593).

Four mechanisms have been suggested for this migration of energy.

(1) *Sensitized fluorescence*: This phenomenon was first observed in gases. The theory was later developed quantum-mechanically (223) and found to agree well with experimental results on dye solutions. The energy is supposed to be transferred by quantum-mechanical resonance from a solvent molecule to a distant solute molecule, molecules intermediate between the two playing no part in the transfer.

(2) *Exciton transfer*: This concept originated in work on energy transport in crystals. A rapid transfer of energy from molecule to molecule is envisaged, the energy residing in any particular molecule for less time than the period of one vibration. A strong coupling of the molecules appears to be necessary for this process (232).

(3) *Photon transport*: On this concept radiation is emitted by a solvent molecule, the radiation being ultimately absorbed by a solute molecule, which then emits its own characteristic radiation (1, 353).

(4) *Photon cascade*: This theory differs essentially from that of photon transport in that it concerns a postulated fluorescence emitted by a solvent molecule, in transitions from higher excited states to the first excited state. Such transitions should occur very rapidly ( $10^{-11}$ – $10^{-12}$  sec.), and experiment indicates that if they occur at all they must be 100 per cent efficient. The emitted radiation (which may be of very much shorter wavelength than that resulting from transition between the first excited state and the ground state) is strongly absorbed by neighboring solvent molecules, whereupon the process is repeated, each transition entailing a loss of energy by degradation of vibrational energy, until molecules result having electronic energy in the first excited state. Normal fluorescence then occurs, and either this characteristic radiation, or the shorter wavelength radiation from one of the earlier stages, is absorbed by solute molecules. These then emit their own fluorescent radiation (59, 60).

Discussions of the arguments for and against these theories, covering the work up to 1953, have already been presented (59, 161). The present position seems to be one in which sensitized fluorescence is rejected and photon transfer is acknowledged to occur but is thought to be trivial; whilst it is still difficult to decide between the photon cascade and the exciton mechanisms, the former seems generally more acceptable. Recent work on energy transfer in (a) 9-phenylanthracene-9,10-dichloroanthracene, (b) 1-chloroanthracene-perylene (68), and (c) the latter mixture dissolved in a glass of tetrachloro- and pentachloroethanes at  $-183^{\circ}\text{C}$ . (69) only shows that simple photon transfer alone cannot explain the facts. In polystyrene-anthracene mixtures photon transfer can explain the results at concentrations of anthracene  $< 5 \times 10^{-4} M$ ; above this concentration the improved efficiency of energy transfer could be due either to exciton transfer or to photon cascade (354).

After long periods of irradiation scintillating systems lose their fluorescence efficiency, and this has been attributed to chemical decomposition (61, 64), as a result of which the products act as fluorescence-quenching agents. Attempts have been made to correlate chemical effects with scintillation effects. Since *p*-terphenyl in benzene behaves as a highly efficient scintillator, it was suggested

that it might also act as an efficient protecting agent for benzene against ionizing radiation (407). This was not borne out by experiment (91), a result which is hardly surprising as the efficiency of energy conversion is  $>0.2$  per cent for the benzene decomposition, and about 1.4 per cent for the scintillation. Moreover, as the authors point out, the energy used in producing scintillations may not lead to decomposition in any case, a suggestion since shown to be highly probable (498). *m*-Terphenyl, which could be used in higher concentration, showed a significant protective effect. Scintillation measurements on solutions of *p*-terphenyl in mixtures of benzene and cyclohexane showed a greater fluorescence yield in deaerated solution than would be expected by adding the effects in benzene and cyclohexane alone (88), but these results, and others in the presence of oxygen, could not be interpreted quantitatively.

(e) Mixtures with water

Irradiation of saturated aqueous benzene solutions with x-rays or  $\gamma$ -rays in the absence of air gives rise to phenol, biphenyl, terphenyl, hydrogen peroxide, and hydrogen (47, 570, 572, 595). Marked differences in absolute yields were

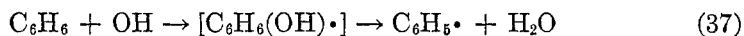
TABLE 4  
*Radiation yields from air-free aqueous solutions saturated with benzene*

<i>G</i> (phenol)	<i>G</i> (biphenyl) (neutral)	<i>G</i> (biphenyl) (0.1 <i>N</i> NaOH)	<i>G</i> (H <sub>2</sub> )	<i>G</i> (H <sub>2</sub> O <sub>2</sub> ) (neutral)	<i>G</i> (H <sub>2</sub> O <sub>2</sub> ) (acid)	Radiation	Reference
0.45	0.6	—	0.63	—	—	200 kvp x-rays	(572)
0.29	0.5	0.38	—	0.25	0.51*	190 kvp x-rays	(47)
0.29	—	—	—	0	0.64† 0.58	Co <sup>60</sup> $\gamma$ -rays	(595)

\* In 0.8 *N* sulfuric acid.

† In 0.1 *N* sulfuric acid.

obtained by different workers, as can be seen from table 4, but it is clear that under these conditions biphenyl is formed in larger yields than is phenol. The effect of pH on the phenol yield is only slight, as might be expected if the mechanism were a free-radical one (47, 572). On the other hand, the yield of biphenyl is significantly lower at high pH (47), and this result is difficult to understand. The mechanism which best fits the experimental results is the following (572):



the small amount of terphenyl probably being formed by the following reactions:

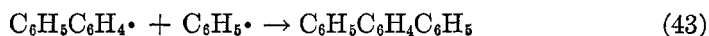
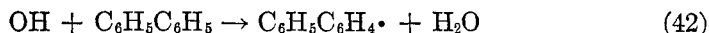


TABLE 5  
*Radiation yields from aerated aqueous solutions saturated with benzene*

Dose Rate	Radiation	G(phenol)	G(H <sub>2</sub> O <sub>2</sub> )	Reference
<i>r/min.</i>				
3000	X-rays (200 kvp)	2.25	—	(572)
3000	X-rays (200 kvp)	—	5.5	(618)
700	X-rays (190 kvp)	1.32	2.14	(47)
4500	$\gamma$ -Rays (Co <sup>60</sup> )	2.7	2.7	(564)
18.3	$\gamma$ -Rays (Co <sup>60</sup> )	3.05	—	(234)
1200	$\gamma$ -Rays (Co <sup>60</sup> )	2.2	2.2	(546)
	$\gamma$ -Rays (Co <sup>60</sup> )	2.6	2.8	(565)
333	X-Rays (23 mevp)	2.74	—	(234)

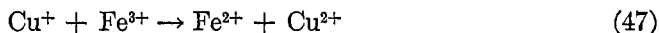
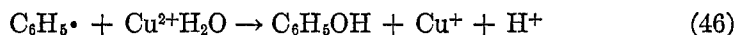
Nevertheless there are difficulties. According to the above mechanism, for example, it would be expected that the proportion of biphenyl would vary with change of dose rate. Such is not the case, and it has been suggested that this might be a consequence of the reaction taking place in localized regions or "tracks" (47).

With neutron or  $\alpha$ -particle irradiation in air-free solutions there is evidence of the formation of hydroquinone and pyrocatechol and of ring opening to give an unidentified dialdehyde (573), in addition to the products obtained with x-rays and  $\gamma$ -rays. Such effects were attributed to the higher linear energy transfer of the  $\alpha$ -particles and the recoil protons ejected by the neutrons. The yields of hydrogen and hydrogen peroxide from aqueous solutions of benzene are also higher with  $\alpha$ -particle irradiation than with x-ray irradiation [ $G_{\alpha}(\text{H}_2) = 1.75$ ;  $G_{\alpha}(\text{H}_2\text{O}_2) = 1.2$ ] (365).

In aerated solutions the yields of phenol and hydrogen peroxide are increased, and that of biphenyl is completely suppressed. The production of phenol under these conditions has been suggested as a method of dosimetry (104, 188), but there is some uncertainty in the yield of the reaction (see table 5). The lack of production of biphenyl implies that a reaction of the type



must occur, and the phenol yield may also be increased by the effect of the HO<sub>2</sub> radical. The yield of phenol is linear with dose until the oxygen in the solution has been used up. At this point (the so-called "oxygen break") the yield falls to just a little above the yield in air-free solution. Another way in which the yield of phenol may be increased at the expense of biphenyl production is by the addition of ferric and cupric ions in small amounts to the irradiated mixture, even when this is air-free (47). The much less marked effect of ferric ion alone suggests the occurrence of very rapid reactions of the following type:



It has been claimed that after the irradiation of aerated solutions of benzene with  $\text{Co}^{60}$   $\gamma$ -rays or in the pile is stopped, phenol continues to be formed and hydrogen peroxide disappears (633). This effect was not observed with x-rays (47). In the presence of hydrogen the yield of phenol is reduced (573), presumably owing to the reaction:



The irradiation of saturated solutions of water in benzene gave no measurable yield of phenol (547).

The only other aromatic hydrocarbon which has been irradiated in aqueous solution is toluene. The products of the  $\gamma$ -ray irradiation of toluene in the presence of water and air were benzoic acid, benzaldehyde, and formic acid, the yield of toluene conversion being  $-G_\gamma(\text{toluene}) = 0.7$  (326, 328).

#### (f) Halogenation

Two aromatic hydrocarbons have been irradiated in the presence of halogens: benzene and toluene. Early work with chlorine, benzene, and  $\alpha$ -particle (12) or x-ray irradiation (393) showed that an addition reaction of chlorine to benzene is favored, and the high yield with  $\alpha$ -particles [ $-G_\alpha(\text{Cl}_2) \sim 2160$ ] indicated a chain reaction. Benzene was also shown to react with iodine under x-ray irradiation, but no products were isolated (138). The electron irradiation of a mixture of benzene vapor and fluorine yielded 87 per cent polyfluorocyclohexane, and from a mixture of chlorine, hydrogen chloride, and benzene vapor a 75 per cent yield of hexachlorobenzene was produced (204).

Recently the study of the chlorination of air-free liquid benzene and toluene, under the influence of  $\gamma$ -rays, has been undertaken (79, 273, 274, 275). With benzene a rapid addition reaction to form an isomeric mixture of 1,2,3,4,5,6-hexachlorocyclohexane occurred, and the temperature could not be controlled. Greater control of the reaction was achieved by chlorination in carbon tetrachloride solution, and under these conditions the reaction evidently proceeded by a chain mechanism [ $G_\gamma(\text{C}_6\text{H}_6\text{Cl}_6) \sim 85,000$  for 20 per cent benzene in carbon tetrachloride]. Such results agree quite closely with those obtained from the ultraviolet irradiation of benzene and chlorine. With toluene this is no longer true, for whereas ultraviolet irradiation gives rise to side-chain substitution,  $\gamma$ -ray irradiation leads predominantly to addition in the nucleus, again to the 1,2,3,4,5,6-hexachloro product, as well as to side-chain substitution to benzyl chloride and benzotrichloride. There is also formation of a little heptachloromethylcyclohexane. The addition product is again formed via a chain reaction [ $G_\gamma(\text{C}_6\text{H}_5[\text{CH}_3]\text{Cl}_6) = 14,000$  to 18,000], which is inhibited by benzyl chloride. The effect of the latter on the substitution reaction is less marked. Other factors which favor the substitution are (1) low chlorine concentrations (the addition reaction is  $\propto [\text{Cl}_2]^2$ ; the substitution reaction is  $\propto [\text{Cl}_2]^{1/2}$ ), and (2) increase of temperature.

The exact mechanism of the reactions is unknown, but the difference between the photochemical and the radiation-chemical effect may arise from a

fundamentally different primary act. The primary act of the photochemical effect is the formation of chlorine atoms



In the radiation reaction it is more likely to be ionization and excitation of the toluene, and possibly electron capture by the chlorine followed by ion neutralization.

### (g) Other mixtures

A mixture of benzene vapor and oxygen irradiated with  $\gamma$ -rays yielded phenol, with a yield of approximately  $G_r(\text{phenol}) = 214$  (208). This high yield indicates that the reaction proceeds by a chain mechanism. The  $\gamma$ -ray irradiation of liquid toluene in the presence of oxygen yielded benzoic acid, benzaldehyde, and formic acid, benzaldehyde being in highest yield and  $-G_r(\text{toluene}) = 3.6$  (326, 328). An unidentified oxidation product was obtained from the prolonged  $\gamma$ -ray irradiation of benzpyrene in hexane solution in the presence of air (436).

Nitration of toluene to 95 per cent *p*-nitrotoluene and 5 per cent *m*-nitrotoluene may be achieved by subjecting a suspension of aluminum oxide in toluene to bombardment with 1 m.e.v. electrons, whilst blowing in a mixture of nitric oxide and oxygen (204).

## 2. Pure hydrocarbons

Owing to their resistance to radiation, it is not easy to study the decomposition of pure aromatic hydrocarbons unless high dose rates are available; hence such studies have almost always been made either with electron beams or with heavy-particle radiations, which are totally absorbed even by the vapors.

### (a) Benzene

This compound has been investigated in the vapor phase under  $\alpha$ -particle irradiation (295, 452), and in the liquid and vapor phase under irradiation with electrons of various energies (83, 262, 412, 468, 525). In both cases the yield of polymer is higher than the yield of gas, and the gas is almost entirely hydrogen and acetylene. Table 6 gives the best values for the yields obtained.

Whether the differences observed between the yields from the liquid and the vapor are due to an effect of state, or to differences of linear energy transfer, is

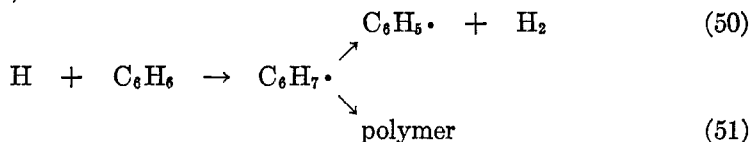
TABLE 6  
*Radiation yields from pure benzene*

Radiation	State	Total Yield ( $G^1$ )	$G$ (polymer)	$G(\text{H}_2)$	$G(\text{C}_2\text{H}_2)$	$G(\text{CH}_4)$	$G(\text{C}_2\text{H}_4)$	$G(\text{C}_2\text{H}_6)$	References
$\alpha$ -Particles	Vapor	—	$\leq 3.6$	—	—	—	—	—	(452)
$\alpha$ -Particles	Vapor	4.9	4.14	0.30	0.42	0.01	0.02	0.006	(295)
0.54 m.e.v. electrons	Vapor	—	—	0.011	0.11	*	0.05	0	(412)
1.5 m.e.v. electrons	Liquid	0.805	0.75	0.035	0.020	0	0	0	(262, 468)

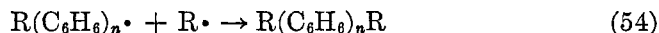
\* Methane may be included in the hydrogen yield.

uncertain; probably both play a part. Little is known of the nature of the "polymer" produced from benzene. This non-volatile product is a viscous yellow liquid (452, 468) and is certainly a mixture; it probably contains biphenyl (468), and it also contains substances with aliphatic double bonds. The average molecular weight increases as the duration of the irradiation increases, the maximum observed value being  $\sim 530$  (468).

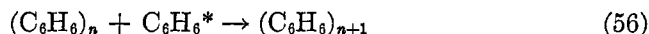
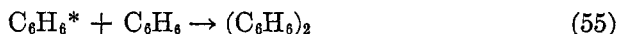
No clear-cut mechanism for polymer formation has been established, but arguments have been advanced for supposing the following reactions to occur in the liquid state (468):



Rate of reaction 51/rate of reaction 50 = 7.3 (469). In the gaseous state hydrogen atoms are more likely to attack benzene to give methane, ethane, ethylene, acetylene, etc. (412). Though the nature of the radical  $\text{C}_6\text{H}_7\cdot$  is unknown, polymer production involves the initial formation of double bonds, and this would arise if the  $\text{C}_6\text{H}_7\cdot$  radical were a hexatrienyl radical. Two alternative mechanisms of polymer formation (reaction 51) have been suggested, both involving excited states of benzene,  $\text{C}_6\text{H}_6^*$ , which are excited with a fixed probability to a definite low energy level (468).



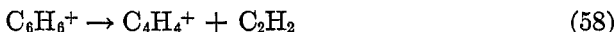
where  $\text{R}\cdot = \text{H}$ ,  $\text{C}_6\text{H}_5$ , or  $\text{C}_6\text{H}_7$ ; or



Reaction 50 probably does not involve the state  $\text{C}_6\text{H}_6^*$ , and it would be expected to yield a certain proportion of biphenyl whichever mechanism of polymer formation were operative.

Interesting conclusions regarding the decomposition to gaseous products resulted from an investigation on benzene, hexadeuterobenzene, and mixtures of the two (262). Mass spectrometric data on the two compounds indicate that the mechanisms of formation of the ions  $\text{C}_6\text{H}_x^+$  and  $\text{C}_m\text{H}_n^+$  ( $m < 6$ ) are different. The essential difference between  $\text{C}_6\text{D}_6$  and  $\text{C}_6\text{H}_6$  is the higher zero point energy of the latter, and since the proportion of the ions  $\text{C}_m\text{H}_n^+$  and  $\text{C}_m\text{D}_n^+$  is the same, their mechanism of formation must be independent of zero-point energy. This implies that they are formed by a rearrangement process, probably from the parent ion  $\text{C}_6\text{H}_6^+$  (or  $\text{C}_6\text{D}_6^+$ ). On the other hand, ions of the type  $\text{C}_6\text{H}_x^+$  and  $\text{C}_6\text{D}_x^+$  occur in different proportions of the total, and are thus considered most likely to be formed by successive loss of hydrogen or deuterium atoms from the

parent ion. Under the conditions of irradiation, i.e., the liquid state in this case, it might be expected that  $C_6D_6$  would give lower decomposition yields than  $C_6H_6$ , owing to the fact that more time will be required for a rearrangement of the parent ion, and more energy for a fracture. This was in fact found: e.g.,  $G_e(D_2) = 0.0117$ ;  $G_e(C_2D_2) = 0.0133$ . The most significant result here is that for  $C_6D_6$   $G_e(D_2) < G_e(C_2D_2)$ , whilst for  $C_6H_6$   $G_e(H_2) > G_e(C_2H_2)$ . This at once suggests that both products are formed by two different mechanisms, which contribute differently in the two cases. The results have been shown to be consistent with one mechanism being a free-radical mechanism and the other being a rearrangement mechanism (262) (see also page 502). Nevertheless the actual mechanism of the decomposition to gas is still a matter for conjecture. The low radiation-chemical yields are paralleled by the low quantum yields in the photochemical reaction. The latter result indicates a long lifetime of the excited state, due without doubt to the non-localization of the excitation energy in a  $\pi$  orbital of the molecule. Similar considerations probably apply to the principal ion formed from benzene, i.e.,  $C_6H_6^+$  (83), the excess energy being dissipated, especially in the liquid, before the  $C_6H_6^+$  ions can decompose to smaller ions. If the ion survives decomposition and is ultimately neutralized by electron capture, the excitation energy will not be very large (9.4 e.v.), and again it may be dissipated before any breakdown occurs. For this reason it has been suggested that ions other than  $C_6H_6^+$  are the ones most likely to contribute to decomposition (83). On the other hand the proportion of such ions, as indicated by mass spectrometry, is significantly higher than would be implied by the radiation decomposition and polymerization yields in the liquid state (262). Two possible reasons for this have been suggested. Firstly, ions of the type  $C_6H_x^+$  may react favorably with H or  $H_2$  to give the stable  $C_6H_6^+$  ion, provided means were present to remove the excess energy (83). Secondly, there may be a tendency, under the conditions of radiation-chemical experiments, for lower ions of the type  $C_6$ ,  $C_5$ ,  $C_4$ ,  $C_3$ , and  $C_2$  not to form at all. In view of the fact that all such ions appear to originate from excited  $C_6H_6^+$  ions, and that they all have higher appearance potentials than these, there should be a fair probability of the excess energy of the parent ion being dissipated, especially in the liquid state, before it can decompose to smaller ions. The results with benzene and hexadeuterobenzene, and the relative yields of  $C_6H_5^+$ ,  $C_6H_4^+$ , and ions of  $C_4$ , as indicated by mass spectrometry (262, 467), suggest that the following processes (233), and corresponding reactions for highly excited benzene molecules, are likely to be of importance:



(b) Other hydrocarbons

The addition of an aliphatic side chain to a benzene ring gives a compound which is more sensitive to radiation than the original benzene. Nevertheless the



TABLE 7  
Relative gas yields from irradiated liquid aromatic hydrocarbons

	Gas Yields Relative to Benzene with 170 kv. Electrons (525)	Gas Yields Relative to Benzene with 1.5 m.e.v. Electrons	$G(\text{gas})$ with 1.5 m.e.v. Electrons
Anthracene.....	0.23	—	—
Naphthalene.....	0.23	—	—
Biphenyl.....	0.23	—	—
Phenanthrene.....	0.23	—	—
$\alpha$ -Methylnaphthalene.....	0.32	—	—
Diphenylmethane.....	0.36	—	—
Triphenylmethane.....	0.41	—	—
$\beta$ -Methylnaphthalene.....	0.41	—	—
Benzene.....	1.0	1.0	0.055*
Phenylcyclohexane.....	1.05	—	—
Toluene.....	1.2	2.55	0.14†
Tetrahydronaphthalene.....	1.2	—	—
<i>p</i> -Cymene.....	1.6	—	—
Hexamethylbenzene.....	3.4	—	—
<i>tert</i> -Butylbenzene.....	—	3.45	0.19‡
Ethylbenzene.....	—	3.8	0.21†
Isopropylbenzene.....	—	4.5	0.25‡
Mesitylene.....	—	4.7	0.26†

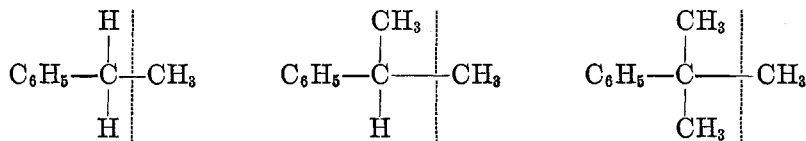
\* Reference 262. † Reference 296. ‡ Reference 597.

result predicted by the statistical principle (85)—that the effect should be directly proportional to the number of aliphatic carbon atoms added—is not always borne out. Table 7 shows the relative gas yields from a number of liquid aromatic hydrocarbons bombarded with 170 kv. electrons (525) and with 1.5 m.e.v., or 1.8 m.e.v., electrons (89, 262, 296, 597). Except for benzene, the evolved gas consists in each case of a mixture of hydrogen and methane, in which hydrogen is the major component. The proportions of methane and hydrogen deviate from the statistical expectation, and the nature of the deviation indicates that there is some transfer of energy from the ring to the side chain, sensitizing decomposition of the latter in the same way as in the photochemical effect. On the other hand the overall gas yields are much lower than those obtained from corresponding aliphatic compounds, indicating that the benzene ring protects the side chain by transferring energy to itself and subsequently dissipating it without reaction in the manner typical of benzene. This "sponge-type" protection is predominant. The two effects are the precise intramolecular analogs of the intermolecular protection and sensitization effects already discussed in the section on mixtures.

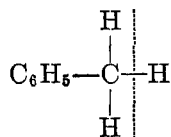
The low gas yields may also be due, in part, to the absorption of hydrogen atoms and other radicals by the ring to give polymers, as with benzene itself. The yield of polymer from toluene is  $G_e(\text{polymer}) = 0.92$  (412), which again is more significant than the yield of gaseous products, and there is evidence of polymer formation in several other alkylbenzenes (102). No other information is available, however, on this important process.

In the photochemistry of alkylbenzenes, transfer of energy, with low probability, from the ring to the side chain results preferentially in the break of a

bond once removed from the ring (89). Mass spectrometry indicates that the same bond is preferentially broken in the parent ion,  $C_7$  ions being most commonly formed from monoalkylated benzenes (467), with a 60–75 per cent probability of loss of a methyl group in the cases of ethylbenzene, isopropylbenzene, and *tert*-butylbenzene (597). Thus the expected types of break are represented as:



But for toluene we might expect (466),



This shows at once why the yields of methane from ethylbenzene, isopropylbenzene, and *tert*-butylbenzene are proportional to the numbers of methyl groups in the molecule, whilst for toluene and mesitylene this is far from being the case.

## B. OTHER COMPOUNDS

The data available on the free-radical yields from the  $\gamma$ -ray irradiation of aromatic compounds other than hydrocarbons are presented in table 8 (results for benzene are given as a comparison). The values in brackets are approximate only and assume  $-G^R_\gamma(C_6H_6) = 1.47$ .

### 1. Pure compounds

From the radiation-chemical viewpoint very few pure aromatic compounds have been investigated at all, and even fewer have been investigated in a quantitative manner. All are comparatively unreactive. Benzoic acid is decarboxylated in low yield by irradiation with deuterons (72) or with  $\text{Co}^{60}$   $\gamma$ -rays (610). There is an equivalent amount of polymer formation. Phenyl iodide yields iodine under

TABLE 8  
Primary radical yields per 100 e.v. ( $G^R$ ) from the  $\gamma$ -ray irradiation of aromatic compounds

Benzene	Nitrobenzene	Chlorobenzene	<i>o</i> -Dichlorobenzene	Aniline	Benzyl Alcohol	Benzylamine	Method	References
1.2	—	12.2	—	—	—	—	Polymerization	(108)
(1.47)	—	—	—	( $\geq 23$ )	( $\geq 88$ )	( $\geq 94$ )	Polymerization	(110)
1.47	—	14.7	—	—	—	—	Polymerization	(408, 489)
1.04	2.57	9.8	17.5	—	—	—	DPPH*	(108)
1.47	3.69	14.0	24.6	—	—	—	DPPH	(408, 489)

\* Diphenylpicrylhydrazyl.

$\gamma$ -ray irradiation (584), but phenyl bromide yields hydrogen bromide (538). The change brought about in phenyl chloride was not ascertained, but benzene was not formed (208). From the x-ray irradiation of solid benzophenone diazide, nitrogen is evolved and diphenyltetrazole is left (258). Pyridine oxalate, on bombardment with neutrons, yields carbon monoxide, carbon dioxide, phenol, and benzene (254). Pyridine (516) and nitrobenzene (208) have been irradiated with x-rays or  $\gamma$ -rays, and show low yields of conversion to unknown products. The pile irradiation of solid *l*-mandelic acid yields benzaldehyde as the principal product (633).

## 2. Non-aqueous mixtures

There is hardly any reaction when mixtures of chlorine with benzyl chloride, benzal chloride, or benzotrichloride are irradiated with  $\gamma$ -rays; in fact, the first of these compounds can completely inhibit the chlorination of benzene by this method (274, 275). The addition and substitution chlorination of toluene may likewise be inhibited, but the effect on the addition is most marked. The  $\gamma$ -ray irradiation of mixtures of chlorine and chlorobenzene yields heptachlorocyclohexane as the principal product with  $G_\gamma = 43,000$ . This implies a chain mechanism (274, 275).

1,1-Di(*p*-methylphenyl)-2,2,2-trichloroethane, 1,1-di(2,4-dimethylphenyl)-2,2,2-trichloroethane, 1,1-di(*p*-chlorophenyl)-2-chloroethene,  $\gamma$ -hexachlorocyclohexane, *p*-dichlorobenzene, hexachloroethane, and chloroform have been irradiated in aerated alcohol and acetone solutions with x-rays (440, 441, 442, 443). In every case hydrochloric acid was produced in yield proportional to the dose, the yields in acetone solution being about 20 per cent less than those in alcohol. The reactions are indirect at low concentrations of the halogenated compounds, but showed indication of becoming direct at high concentrations. Addition of water up to 25 per cent by volume in the solvent has no effect on the yields. This may be due either to an efficient transfer of energy from water to alcohol, or simply to the generation of reactive entities producing identical effects. The yields of hydrochloric acid from the compounds studied show a good statistical correlation with the numbers of chlorine atoms, and the strengths of the different types of C—Cl bonds (409). Other possible products were not investigated.

The irradiation of benzoic acid-alcohol mixtures with electrons produces good yields of salicylic acid (204), but the esterification of benzoic acid with ethanolic hydrogen chloride was unaffected by  $\gamma$ -ray irradiation (320).

Quinoline (334), pyridine, aniline, nitrobenzene, and *o*-nitrotoluene (331) have all been irradiated with  $\gamma$ -rays in the presence of oxygen. Yields were established from changes in density, conductivity, or acidity and were found to be:  $-G_\gamma(\text{quinoline}) = -G_\gamma(\text{nitrobenzene}) = -G_\gamma(\text{o-nitrotoluene}) = 0.4$ ;  $-G_\gamma(\text{pyridine}) = 1.1$ ;  $-G_\gamma(\text{aniline}) = 1.4$ . The products from pyridine, aniline, and *o*-nitrophenol were unidentified; from quinoline an aldehyde was produced; and *o*- and *p*-nitrophenol were formed from nitrobenzene.

Mixtures of dried and degassed pyridine and carbon tetrachloride gave effects under x-ray irradiation which were not the additive results expected from the

effects on the pure components (516). The mixture was more sensitive to radiation, but insufficient data are at present available to suggest the reason for this.

The  $\gamma$ -ray irradiation of *o*-nitrobenzaldehyde in either aerated ethanol or benzene solution caused the production of acid, possibly by isomerization to *o*-nitrosobenzoic acid (320). The approximate yield was  $G_{\gamma}(\text{acid}) = 1.4$ . Solutions of quinone in aerated ether or alcohol solution were apparently unchanged by  $\gamma$ -ray irradiation (320).

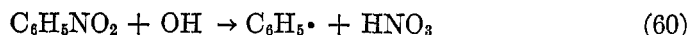
The  $\gamma$ -ray irradiation of mixtures of chlorobenzene and hydrogen gave what was thought to be hydrogenation, without the formation of benzene (208).

### 3. Mixtures with water

A prolonged irradiation of benzoic acid in aqueous solution with  $\gamma$ -rays gave yields of formic and oxalic acids which could be isolated (327). These products have not been found in more recent investigations with 200 kvp x-rays at higher dose rates (392, 572). It was found that in air-saturated solutions all three isomeric hydroxybenzoic acids were formed. Small amounts of biphenyl and phenol were also detected, but no attempt was made to find biphenyldicarboxylic acids. Sodium benzoate in aqueous solution also yielded phenolic products under x-ray irradiation (188). Very similar results were obtained with nitrobenzene and chlorobenzene in aqueous solution. Early work indicated the formation of *o*- and *p*-nitrophenol when moist nitrobenzene was irradiated with radium  $\beta$ -particles and  $\gamma$ -rays (331). Later work with x-rays showed that all three hydroxylated isomers are formed (391), and the same is true of chlorobenzene (318). However, with phenol in aerated aqueous solution x-ray irradiation yields only the ortho and para dihydric phenols (575).

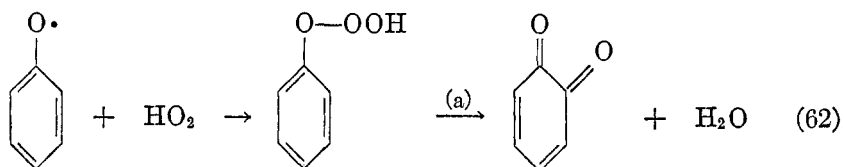
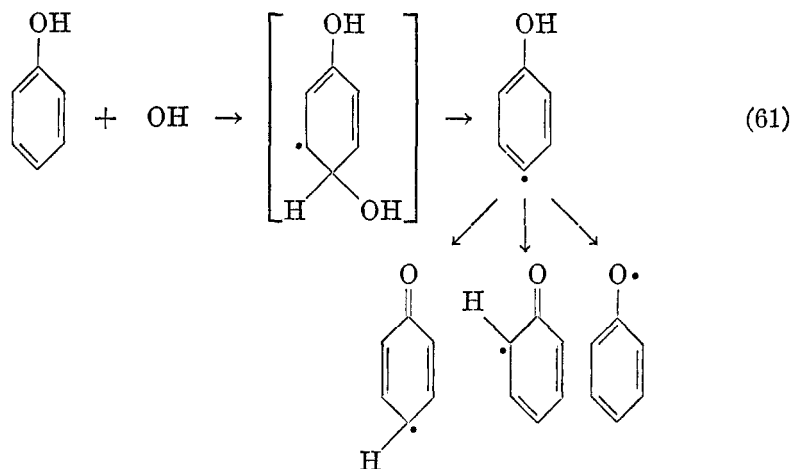
In the cases of nitrobenzene, chlorobenzene, and phenol, an attempt has been made to show that the mechanism of reaction in irradiated aqueous solutions is a free-radical one, by comparing the results with those obtained using the Fenton reagent ( $\text{Fe}^{2+}/\text{H}_2\text{O}_2$ ). The results are parallel, inasmuch as the same isomers are obtained by both methods, but quantitative comparisons of the ratios of isomers show quite marked differences (see table 9). There are two possible reasons for this. Firstly, it is assumed that the  $\text{HO}_2$  radical, presumably formed in irradiated aerated aqueous solutions, behaves in an exactly corresponding manner to the OH radical in all its reactions, and this may not be the case. Secondly, the presence of ferrous and ferric ions in the Fenton experiments may well lead to oxidative and reductive reactions involving these ions, for which there is no counterpart in the radiation experiments. This is particularly noticeable in the Fenton oxidation of phenol, where, in order to obtain reproducible results, agents which form complexes with ferric ion must be added to the mixture, and where, in the absence of such agents, the yield of catechol becomes greater than that of quinol (575). Nevertheless the results are consistent with a free-radical mechanism. The occurrence of biphenyl in the products from benzoic acid and chlorobenzene, and of 3,3'-dinitrobiphenyl in the products from nitrobenzene, is an indication of the operation of mechanisms of hydroxylation exactly paral-

lel to that already discussed for benzene. Reactions involving the side group also occur. Nitric acid is produced from nitrobenzene, probably by the reaction



The phenyl radical would then provide the source of phenol formed. Similarly with chlorobenzene there is some dechlorination, and attack of this kind probably explains the yields of formic acid from benzoic acid, to which reference was made above. Dehalogenation by irradiation in aqueous solution has also been observed in the following aromatic compounds: bromobenzene (and chlorobenzene), *o*- and *p*-dichlorobenzene (439), *o*- and *p*-dichlorophenol (443). It was claimed that hexachlorobenzene is not so dehalogenated (449), and this may indicate that the effective process necessitates the presence of a hydrogen atom attached to another carbon atom in the molecule.

The behavior of aqueous solutions of phenol on irradiation is undoubtedly more complex than that of benzoic acid, chlorobenzene, or nitrobenzene. Thus *o*-benzoquinone is also formed, and appears to arise by a mechanism independent of the other products. A suggested mechanism is the following (575):



The last step may be comparatively slow, and processes of this kind may well be responsible for certain radiation-chemical syntheses which have been reported (355, 396, 397). All such syntheses have to be carried out in aerated solutions and involve either a phenolic compound or an aromatic compound from which a phenol may first be produced by irradiation. Several phenolic compounds (gallic

TABLE 9

*The relative yields of isomeric hydroxylation products from aromatic compounds irradiated with 200 kvp x-rays in aerated solutions, and from reaction with Fenton's reagent*  
(Results in brackets apply to air-free solutions)

Compound	pH	Fenton's Reagent			X-rays			Reference
		<i>o</i>	<i>m</i>	<i>p</i>	<i>o</i>	<i>m</i>	<i>p</i>	
Benzoic acid.....	3	—	—	—	0.5(0.4)	0.2	1.0(1.0)	(392)
Nitrobenzene.....	Low	0.56	0.44	1.0	—	—	—	(390)
	2	—	—	—	1.0	0.9	1.0	(391)
	6	—	—	—	1.0	0.82	1.0	(391)
	12	—	—	—	0.60	0.59	1.0	(391)
Chlorobenzene.....	1	1.0	~0.53	~0.53	—	—	—	(318)
	2	—	—	—	0.73	0.87	1.0	(318)
	6	—	—	—	0.32	0.41	1.0	(318)
	12	—	—	—	1.0	0.60	1.0	(318)
Phenol.....	2	—	—	—	0.24 (0.21)	0	1.0	(575)
	6	—	—	—	0.67 (0.50)	0	1.0	(575)
	12	—	—	—	0.38 (0.25)	0	1.0	(575)
	—	0.35	0	1.0	—	—	—	(575)

acid, tannin, adrenaline, and tyrosine) showed a small increase in optical density immediately after x-ray irradiation in aerated aqueous solution, but on standing the optical density continued to increase, the rate of increase being accelerated by copper ions, heat, or light (398, 403). Such an effect probably corresponds to reaction 62a above and may be prevented by the addition of thiourea, cysteine, or ascorbic acid immediately after irradiation.

The ultimate result of reaction 62a depends very largely on the size and complexity of the molecule concerned. With molecules of large molecular weight there seems to be a high probability of the peroxide group reacting with another part of the molecule and disrupting it, after irradiation (see section on nucleic acids) (page 549). With fairly simple aromatic compounds the peroxide may take part in coupling reactions with other molecules present, either after or during the irradiation. An example is the synthesis of methylene blue by irradiating a mixture of dimethyl-*p*-phenylenediamine, hydrogen sulfide, hydrochloric acid, and copper sulfate (355). With  $\alpha$ -naphthol or *m*-toluylenediamine, instead of hydrogen sulfide, indophenol or toluylene blue may be formed (396). In each case peroxides are probably formed from the *p*-phenylenediamine and react subsequently with the other materials. The latter may be added after the irradiation, but the yields are then lower. This suggests that the reason why aromatic materials are necessary is to give rise to peroxides which are sufficiently stable to react with other components before spontaneous decomposition. By this technique it is possible to synthesize urea (from methylene chloride, ammonia, and *m*-phenylenediamine) (397). The radiation syntheses of indigo, azo dyes, and aniline dyes (from phenol + amine) (204) probably entail similar processes.

Other aromatic compounds which have been irradiated in aerated aqueous solutions are pyridine [ $-G_r(\text{pyridine}) = 2.5$  (331)] and aniline, nitroaniline,

pyrogallol, resorcinol, and  $\alpha$ - and  $\beta$ -naphthol, mixed with various other substances (137).

#### IV. POLYMERS

In recent years there has been a spate of publications dealing with the chemical and physical effects arising from the irradiation of polymers. Much of the work is empirical in its approach, but latterly certain investigations have given clear indications as to the processes occurring. The most important discoveries have been made with vinyl polymers.

##### A. VINYL POLYMERS

When irradiated in the absence of air such polymers may undergo three principal types of change. They may be cross-linked, the main chains may be degraded, or side groups may be degraded. In no case has the production of the corresponding monomer been reported, probably because the operating temperature has always been too low for the rate of depropagation to be significant (165). An empirical rule has been suggested by which it is possible to predict whether cross-linking, or degradation, will be the predominant feature of the irradiation of any given vinyl polymer (437). According to this rule cross-linking will occur only when the polymer contains at least one hydrogen atom in the

$\alpha$ -position to the  $-\text{CH}_2-$  group: i.e., it is of the form  $\left[ \begin{array}{c} \text{X} \\ | \\ -\text{CH}_2-\text{CH}- \end{array} \right]_n$ . Where this is not the case degradation will be the major effect, degradation of the main chain occurring only if the polymer is of the form  $\left[ \begin{array}{c} \text{CH}_3 \\ | \\ -\text{CH}_2-\text{CX}- \end{array} \right]_n$ .

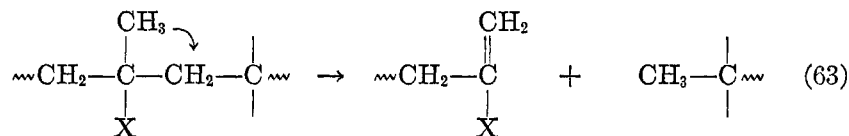
TABLE 10

*The effects of radiation on polymers, and their relation to steric strains*

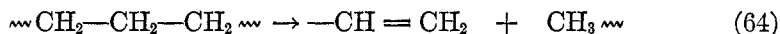
Polymer	Predominant Observed Effects			$\Delta H$ ( $= \Delta H_p$ (obsvd.) $-\Delta H_p$ (calcd.)) (221)	Reference
	Cross-linking	Main-chain degradation	Side-chain degradation		
				<i>cal./mole</i>	
Polythene.....	×			0	(130)
Polymethylene.....	×			—	(437)
Polymethyl acrylate.....	×			1	
Polyacrylic acid.....	×			1.5	(437)
Polystyrene.....	×			2.0, 2.6	(124)
Polypropylene.....	×			3.7	(437)
Polyacrylamide.....	×			—	(437)
Polyvinyl alkyl ethers.....	×			—	(437)
Polyvinyl methyl ketone.....	×			—	(437)
Polymethacrylic acid.....		×		3	(437)
Polymethyl methacrylate.....		×	×	6.2	(4)
Polyisobutylene.....		×		6.1, 6.6	(361)
Poly- $\alpha$ -methylstyrene.....		×		9	(437)
Polymethacrylamide.....		×		—	(437)
Polytetrafluorethylene.....		×		—	(122)
Polyvinyl alcohol.....	×	×		—	(25)

Several factors may contribute to the validity of this generalization: whatever the mechanism, it might be expected that cross-linking would be assisted by an ordered arrangement of polymer chains, in which the carbon skeletons were in close proximity. Such is the case for polyethylene and for polymers containing a single small substituent of a highly polar nature: e.g., CN, OH, or Cl. Conversely, cross-linking may be rendered difficult in polymers containing a large non-polar substituent such as a phenyl group.

The steric factors which tend to prevent cross-linking will often put a premium on main-chain degradation. Large groups introduced into a vinyl polymer chain set up steric strains, and these are manifest as a lower observed heat of polymerization than that calculated assuming no strain to be present (221). Some examples of such differences in relation to radiation effects are shown in table 10. It may also be necessary for main-chain degradation to occur by a rearrangement process, and it has been suggested that this is possible in the following way when one of the substituted groups is a methyl group (25):



The only possible rearrangement in a polymethylene structure, viz.



is likely to be far less ready. The only other groups which are likely to lead to simple rearrangement are hydroxyl, amino, and other alkyl groups. Though all such effects play their part, there are other factors of importance such as the migration of energy, as will be discussed below.

### 1. Polyethylene and related materials

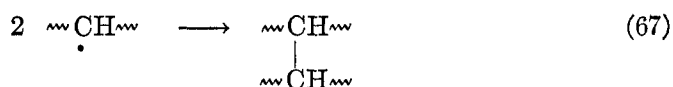
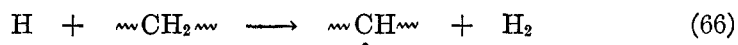
The irradiation of paraffin wax leads to changes which would be expected from the known effects on the lower paraffins, i.e., the production of both cross-linking and main-chain breakage (see section on saturated hydrocarbons). Thus it was early found that low-melting paraffin wax when irradiated with  $\alpha$ -particles evolved large amounts of gas and gave rise to a solid of very high melting point (517). An attempted analysis of the gas from such experiments indicated it to be mainly hydrogen (503). Polyethylene behaves similarly, and approximately the same energy per cross-link was required for pile-irradiated "Polythene" and "Winnothene" (two different types of polyethylene) as for straight-chain hydrocarbons, though the results were less precise (130). The energy required per cross-link, irrespective of the size of the chain, the state of the material, or the radiation employed, is of the order 24 e.v. The ratio of C—C bond breaks to C—H bond breaks in the long-chain polymers is 0.18.

Other work with polyethylene irradiated in the pile (123, 126, 133, 134, 136, 511), with electrons (45, 359, 361), and with  $\gamma$ -rays (29) confirms the general result that polyethylene suffers cross-linkage, main-chain breakage, and loss of

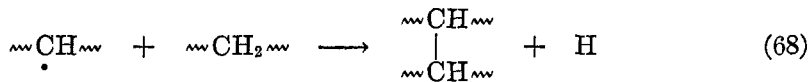


hydrogen on irradiation. There are interesting additional effects due to the branches in polyethylene; thus, although the evolved gas was earlier reported to consist of 98 per cent hydrogen, small amounts of methane and ethane, and only traces of propane and butane (123, 125), it has since been claimed that the yield of methane is negligible, and that there are appreciable yields (amounting to 15 per cent of the total) of C<sub>2</sub>, C<sub>3</sub>, C<sub>4</sub>, and C<sub>5</sub> hydrocarbons, both saturated and unsaturated (362). The difference may be due to the fact that pile radiation was used in the first investigation and an electron beam in the second. It was suggested that these gaseous products arise from short side chains in polythene, of which the most probable length is C<sub>3</sub> to C<sub>5</sub>, but it is not clear why these should disrupt at the branch points, unless the C—C bond energy in this tertiary position is lower than in the main chain. It has been estimated that carbon-carbon bonds in side chains are ruptured much more frequently than those in the main chain, and about half as frequently as carbon-hydrogen bonds (196).

Side chains in polyethylene are also thought to be the seat of much of the cross-linking. With straight hydrocarbon chains the most likely mechanisms for the formation of cross-links were considered to be the following (130):

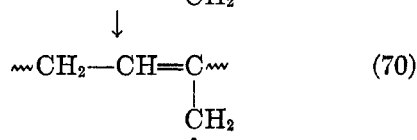
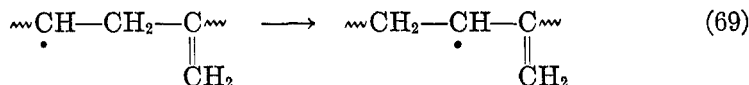


or

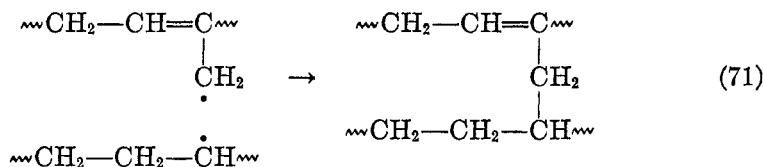


But it is known that the presence of unsaturation in a hydrocarbon tends to increase the proportion of condensed product obtained on irradiation (see section on unsaturated hydrocarbons), and it has been shown that an increasing degree of unsaturation leads to a lower amount of energy required to form a cross-link (132); e.g., the relative values for octadecane, octadecene, and octadecyne are 1:0.66:0.38. Now polyethylene itself possesses some unsaturation, and this is totally in the form of vinylidene groups, there being on the average one vinylidene group per molecule of polyethylene. It has been found that after irradiation of polyethylene in the pile, the number of such vinylidene groups decreases, but simultaneously there is an increase in *trans* vinylene groups (195, 196), a result confirmed by other workers (28). The most significant feature of this work is the fact that for every 3.6 molecules of hydrogen evolved, one vinylidene group was eliminated. As there is only one vinylidene group per 2,300 carbon atoms, this result indicates that chemical activity is migrating over long distances. It has been suggested that the mechanism involves the slow migration of free-radical

centers via random hydrogen-atom transfer (196). The following processes may then occur,



the radical in this last form being supposedly comparatively stable. When an active center formed in another chain nears a point favorable for reaction with this "trapped" radical, cross-linking takes place.



Such a mechanism would account for the formation of some of the vinylene groups, but not all, and some of the hydrogen must be presumed to arise from the formation of unsaturation. In fact it has been variously estimated that 70–80 per cent (196) or 25 per cent (542) of the evolved hydrogen resulted from the production of unsaturation, the remainder coming from cross-linking. As the change from vinylidene to vinylene double bonds is not a *cis-trans* isomerization, there is no obvious connection between this effect and the information regarding *cis-trans* isomerization in irradiated hydrocarbons (see unsaturated hydrocarbons).

The above mechanism for migration of activity is not one on which there is general agreement. In support of it there is the fact that paramagnetic resonance is observed in the irradiated polymer (151), the effect falling rapidly within 4 hr. after irradiation. Moreover, independent evidence for the presence of free radicals in irradiated polymers has been obtained (613), for the intrinsic viscosity of a solution of an irradiated polymer may be changed by dissolution in a solvent containing an inhibitor of polymerization. On the other hand, it is well known that the conductivity of polyethylene increases on irradiation (228, 229, 417, 630), and though the ions produced may be comparatively short-lived, a mechanism of ion transfer along the chain is not entirely ruled out. In some polymers the time taken to recover the original conductivity may be quite long—e.g., for polytetrafluoroethylene, nine months (388); for polystyrene >80 hr. (215); for polyvinylidene chloride, 82 hr. (21)—whilst polyvinyl chloride recovers comparatively quickly (21). There is also the possibility of energy transfer along the chain (see section on aromatic compounds), but the fact that decalin is more efficiently protected by naphthalene substituted at the center of the chain than at the end (2) seems better support for a slow process, such as radical migration, than of a (presumably) rapid process, such as excitation or ionization transfer.

Irradiation of polyethylene in the pile at temperatures near the melting point gives rise to a completely amorphous material after a shorter irradiation time than at lower temperatures (126, 511). A wide variety of materials, differing widely in mechanical properties, can be made in this way.

The irradiation of polyethylene has been used to estimate the molecular weight distribution of the original polymer. The method consists in measuring the sol fraction after irradiating the gel fraction of a previously irradiated polyethylene sample (incidentally giving a positive demonstration of the occurrence of main-chain scission) (44, 45).

## *2. Polystyrene*

The predominant effect of irradiating polystyrene in the pile is to produce cross-linking (124), there being no evidence of significant main-chain breakage. This is in accord with its structure and the principles discussed earlier. The yield of cross-linking is very low (about 100 times less than that for polyethylene (25)), as might be expected with so many benzene rings present to absorb the ionization and excitation energy imparted to the molecule. This is a case of "sponge-type" protection (see aromatic compounds). The rate of cross-linking with  $\beta$ -particle irradiation is apparently proportional to (dose rate)<sup>1/2</sup> (218).

## *3. Polymethyl methacrylate*

As expected from its structure, this polymer is found to break down when irradiated in the pile or with  $\gamma$ -rays (4, 135, 613). Breakdown occurs both in the main chain and in the side chains, at the same rate. The gases evolved are hydrogen, carbon monoxide, carbon dioxide, and methane. The energy required for each break in the main chain is 61 e.v. (2).

## *4. Polyvinyl chloride*

The structure of this polymer would lead to the expectation of cross-linking on irradiation. Changes in mechanical properties after  $\gamma$ -ray irradiation indicate that this expectation is borne out (100, 101, 518), but the viscosity in tetrahydrofuran solution falls (613). In addition there is a considerable evolution of hydrogen chloride (290, 291).

## *5. Polytetrafluoroethylene*

Irradiation of this polymer in the pile gives appreciable carbon-carbon fracture and no evidence of cross-linking (122). Carbon tetrafluoride was produced, but there was no evolution of fluorine. The  $\gamma$ -ray irradiation of the polymer immersed in dilute caustic soda solution gave a material containing the groups  $-\text{CF}=\text{CF}-$  and  $-\text{CF}=\text{CF}_2$ . This was assumed to be caused by the evolution of fluorine (518).

## *6. Other vinyl polymers*

Polyisobutylene shows no cross-linking and is rapidly degraded (186, 361), 17 e.v. being required per main-chain break (2). Polymonochlorotrifluoroethyl-

ene gives evidence of some halogen evolution and main-chain breakage (100, 101). Interesting examples of intermolecular protection have been provided by irradiating polymethyl methacrylate with certain added materials, and an excellent example of intramolecular energy transfer and protection is provided by the irradiation of a copolymer of isobutylene and 20 per cent styrene (4). In this case the energy required per cross-link is 32 e.v., as compared with 17 e.v. for polyisobutylene. The consequences of irradiating copolymers of styrene-vinyl bromide, styrene-*p*-bromostyrene, methyl methacrylate-vinyl bromide, and methyl methacrylate-*p*-bromostyrene are more difficult to interpret (613). Polyvinyl alkyl ethers, polyvinyl methyl ketone, polymethylene, polypropylene, polyacrylic acid, polyacrylamide, poly- $\alpha$ -methylstyrene, polymethacrylic acid, and polymethacrylamide have also been investigated (437).

#### B. OTHER TYPES OF POLYMER

The effects obtained on irradiating many other polymers have been studied, and all such investigations, which mostly concern mechanical properties, cannot be discussed here (66, 81, 203, 361, 386, 518, 554). A decreasing order of the resistance of various polymers to radiation is as follows (554): mineral-filled furan and phenolics, styrene polymers, aniline-formaldehyde polymers, polyvinylcarbazole, polyethylene, nylon, mineral-filled polyesters, unfilled polyesters, phenolics with cellulosic fillers, melamine and urea plastics, unfilled phenolics, vinylidene chloride, methyl methacrylate, teflon, and the cellulose.

Nylon yields hydrogen on irradiation, and groups of atoms are broken off the chains; the degree of crystallinity changes, and a methyl-substituted nylon is apparently formed (387). With polyethylene terephthalate breakdown of the chains is again indicated, and there may be some branching, but there is no evolution of hydrogen or formation of low-molecular-weight materials (387, 606). All these results are at variance with an earlier claim that both nylon and "Terylene" were cross-linked by irradiation (125), but this may be because cross-linking can only be observed with a comparatively low total dose.

Unvulcanized rubber is cross-linked by radiation at a rate higher than for polyethylene (127, 186, 518). This is probably due to the existence of a greater number of double bonds suitable for the formation of cross-links in the rubber. Other materials which are cross-linked are the siloxanes (128, 361). Cellulose acetate suffers decrease of crystallinity and is degraded (629).

#### C. POLYMERS IN THE PRESENCE OF OXYGEN

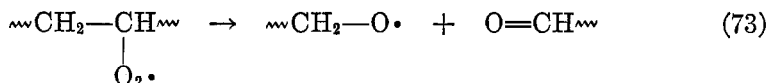
When oxygen is present, there is a tendency for any free radicals, formed during irradiation, to form peroxides by a reaction of the type



rather than to form cross-links. In many cases breakdown of the material is more rapid in the presence of oxygen (386). The breakdown is accompanied by appreciable oxidation, and infrared measurements have indicated that hydroxyl and carbonyl groups are formed in significant amounts (28, 194, 542). With polyethylene there is less oxidation at  $-18^\circ\text{C}$ . than at  $25^\circ\text{C}$ . (28).

It was previously thought that most of these oxidation effects occurred at the surface, and that the effect throughout the bulk of the polymer was not usually marked (66, 129, 196). However, in a recent publication on polyethylene close attention has been paid to the effect of oxygen (114). The oxidation of aerated polyethylene with  $\gamma$ -rays is strongly dependent on the dose rate. At low dose rates, oxygen can diffuse into the bulk of the polymer quickly enough to provide sufficient oxygen for peroxide formation throughout the irradiation. Under these conditions, even very high doses do not yield an infusible polymer. At high dose rates the oxygen in the polymer is rapidly used up and cannot be replaced quickly enough by diffusion to maintain a high rate of peroxide formation. Much of the earlier work was done under these conditions, thereby leading to the conclusion that oxidation tended to occur only at the surface. It was also suggested that previous workers did not take sufficient precautions to deaerate polymers before irradiation, even though the irradiations were done in vacuum or under nitrogen. With adequate deaeration the dose of  $\gamma$ -rays required to produce infusibility was found to be appreciably less than previously reported.

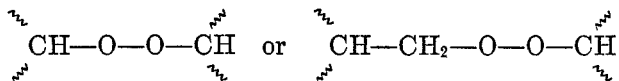
Possible mechanisms (114) for the oxidation of polyethylene are



or



In addition there is evidence of the irradiation in oxygen producing a type of cross-link which breaks down at temperatures higher than 150°C. It has been suggested that such cross-links may be of the following form (114):



#### D. POLYMERS IN SOLUTION

The effects of radiations on polymers in solution are indirect. The first such investigation concerned aqueous solutions of polyacrylic acid and polymethacrylamide (304), x-ray irradiation of the former causing a fall in the pH of the solution, whilst the latter showed no such change. Later work has shown that polymers irradiated in aqueous solution may be degraded or cross-linked, and that the effect observed may depend on the concentration of the polymer (3). Polymethacrylic acid suffers main-chain degradation on irradiation with x-rays in aerated aqueous solution, whatever the concentration (3, 5, 6, 7, 8). In the absence of air no degradation occurs, suggesting that the primary entities formed from irradiated air-free water are not alone capable of inducing this effect. This result, and the fact that hydrogen peroxide causes an enhanced effect in either aerated or deaerated solution, has led to the suggestion that the  $\text{HO}_2$  radical is the entity responsible for the degradation (8). (At pH 7.2, as here employed, most of the  $\text{HO}_2$  would be in the form  $\text{O}_2^-$ , but this does not affect the argument.) The generally accepted mechanism for the formation of the  $\text{HO}_2$  radical

in aerated aqueous solution (reaction 1 or 2) is considered to be supplemented by the addition of hydrogen peroxide in the following way:



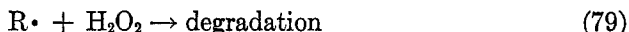
This will occur in either aerated or air-free solution. In air-free solution process 1 is replaced by



together with process 75. A possible alternative scheme of the type



was rejected. However, there seems to be no objection to the following explanation of the potentiating effect of hydrogen peroxide on the degradation. In aerated solution reactions 77 and 78 may be supplemented by reaction 76. In air-free solution the reactions could be 76 and 77, followed by reaction 79:



The fact that hydrogen added to the aerated solution does not potentiate the effect of x-rays by reactions 48 and 1, as would be expected if  $\text{HO}_2$  were the effective entity, lends some support to the above alternative, as do certain results in organic solvents (see below).

Polyvinyl alcohol is cross-linked when irradiated in deaerated aqueous solution but not when irradiated in the presence of oxygen (2). Moreover, at low concentrations of the alcohol (0.3 per cent), even in deaerated solution, the effect becomes one of degradation (3). Similar behavior is exhibited by polyvinylpyrrolidone, polyacrylamide, and polyacrylic acid at low pH (3). At pH 7, polyacrylic acid is degraded at all concentrations, as is also polystyrene sulfonate. In none of the above cases is the mechanism fully understood, but for polyvinylpyrrolidone the results are consistent with the scission of chains into two active portions, which may then form cross-links (so-called "end-linking").

The  $\gamma$ -ray irradiation of polystyrene in carbon tetrachloride or toluene (613) and in chloroform (117, 230) has been studied, and there are also results for the  $\gamma$ -ray irradiation of a copolymer of styrene and vinyl bromide in carbon tetrachloride, toluene, or benzene (613). In all cases the polymer was degraded, and the effect was very much more marked in the presence of oxygen, though some degradation of polystyrene in air-free chloroform was observed (117). Peroxides have been detected in irradiated air-containing solutions of polystyrene in chloroform and may thus be involved as intermediates in the degradation.

## V. ORGANIC OXIDATION-REDUCTION SYSTEMS AND DYES

All the investigations referred to under this heading deal with irradiations of materials in very dilute solution. About sixty such substances have been examined—generally in aqueous solution, less commonly in organic liquids, and

sometimes in the solid phase. Relatively few of the studies have been at all detailed, and in no case has a complete analysis of the products been made. Consequently many of the reported results are concerned only with the disappearance of the solute, an effect generally observed by a change in, or disappearance of, the color of the solution. All the earlier investigations were directed towards finding suitable materials for use in solution dosimetry (137, 577).

#### A. AQUEOUS SOLUTIONS

##### 1. *The effect of oxygen*

Early workers with dyes failed to appreciate the important differences possible in the effects of irradiation with and without oxygen. Thus, although it was reported that a variety of dyes of the thiazine, disazo, indigo, quinone, hydroxyketone, and triphenylmethane classes were bleached by x-ray irradiation in aerated solution (137, 150, 577), some confusion existed as to the nature of the change. The bleaching of such dyes having previously been associated with their reduction, there was a tendency to regard the effect of radiation as such (150), though in no known case of the irradiation of a dye in aerated solution has it been found possible to restore the color of the dye by oxidation. Another point which does not always seem to have been appreciated is that a very high degree of deaeration is required in order to observe the true effects in deaerated solution.

The first work on thoroughly deaerated aqueous solutions showed quite conclusively that the irradiation of a variety of azine, oxazine, thiazine, cyanine, indophenol, indamine, monoazo, and indigo-type dyes with x-rays led in every case to bleaching, which could be partially, but not wholly, reversed by admitting air to the solution (543). This of course implied that under these conditions an appreciable proportion of the dye was reduced to the leuco form, a conclusion receiving some support from work on the x-ray irradiation of benzoquinone followed electrometrically (615). It was claimed that some dyes could not be completely bleached in this way, and an attempt was made to relate this effect to the reversible reduction potentials of the dyes, those dyes having reduction potentials more positive (on the U. S. scale) than potassium indigodisulfonate being the ones which could not be completely bleached.

##### 2. *Methylene blue*

This dye has been the subject of the largest number of investigations in its particular class. As its behavior is probably similar to that of many of the dyes so far studied, the results of these investigations will for the moment be regarded as typical. Three facts seem certain regarding this system: (1) Irradiation in aerated solution gives rise to bleaching by destruction only, any leuco dye which might be formed being rapidly reoxidized to the dye, until the oxygen in the system is consumed (137, 146, 150, 187, 260, 399, 445, 477, 478, 549, 567, 568, 577, 579, 580). (2) Irradiation in fully deaerated solution gives rise to bleaching, partly by reduction to the leuco form, and partly by irreversible changes, presumably of oxidation. Evidence for reduction to the leuco form is provided by the restoration of the dye color on admitting air (187, 476, 543, 567), by electro-

TABLE 11  
*The bleaching of aerated aqueous methylene blue solutions by ionizing radiations*

Radiation	Dose Rate	Concentration of Dye	$G_1$ (bleaching)	Reference
	<i>r/min.</i>	<i>M</i>		
220 kvp x-rays	570	$6 \times 10^{-5}$	0.47	(147)
X-rays	—	$7.5 \times 10^{-6}$ to $6 \times 10^{-5}$	0.12	(445)
100 kv. x-rays	250	$2.6 \times 10^{-5}$	0.22	(549)
200 kvp x-rays	3000	$5.4 \times 10^{-5}$	1.4	(568)
220 kvp x-rays	570	$6 \times 10^{-5}$	1.1	(147)
100 kv. x-rays	250	$1.7 \times 10^{-4}$	0.7	(549)
16 m.e.v. electrons	—	$3 \times 10^{-5}$ to $3 \times 10^{-4}$	1.1	(260)

*The bleaching of air-free aqueous methylene blue solutions by x-rays*

Radiation	Dose Rate	Concentration of Dye	$G_1$ (bleaching)	$G_1$ (leuco form)	$G_1$ (oxidized form)	Reference
	<i>r/min.</i>	<i>M</i>				
120 kv. x-rays	40	$10^{-5}$ to $2 \times 10^{-5}$	0.6	—	—	(246)
200 kvp x-rays	3000	$5.4 \times 10^{-5}$	1.3	0.3	1.0	(568)
220 kvp x-rays	730	$3.6 \times 10^{-5}$ (a)*	1.5	0.9	0.6	(147)
220 kvp x-rays	570	$1.3 \times 10^{-5}$ (b)	2.0	$<1.2$	$>0.8$	(147)
220 kvp x-rays	570	$1.3 \times 10^{-4}$ (b)	2.0	$<1.4$	$>0.6$	(147)

\* Sample (a) was a commercial redox indicator; sample (b) was purified by two recrystallizations from water.

metric measurement (395), and by direct spectrophotometric observation of the production of the leuco form (146). (3) The overall rate of bleaching is higher in air-free solution than in aerated solution. Owing to the low concentrations generally employed, and the difficulty of ensuring exact equivalence of starting materials, quantitative measurements are difficult in these systems (582). The values in table 11 should, therefore, be regarded as approximate only. It is evident that there are sometimes marked deviations between the results obtained by different workers. One yield in air-free solution appears low (246), but the effect of added materials in this work (see below) seems to indicate that the solutions were not fully deaerated. Other conclusions are that the yield in deaerated solution shows little variation with concentration down to  $10^{-5}$  *M* (it was earlier claimed to be independent of concentration down to  $5 \times 10^{-6}$  *M* (543)), and that in both aerated (579) and deaerated solutions (543) the rate of bleaching is slower in acid than in alkali.

A possible explanation of the results on such dyes is the following. In air-free solution the effective radicals H and OH may both be taken up by the dye ions; but whereas H atoms are unlikely to react at any other location in the molecule than that part leading to the formation of semiquinone, and ultimately leuco dye, the OH radicals may react at several positions, in the way previously discussed for aromatic compounds in solution. Each dye ion may therefore take up a maximum of two hydrogen atoms but may account for several OH radicals. Thus the yield of leuco dye initially is likely to be larger than the yield of irreversible product, though ultimately the leuco form itself must be attacked by hydroxyl radicals and converted to irreversible products; this too has been observed (146,



543). Such an effect explains why it is possible to reduce dyes having very highly positive reduction potentials. Contrary to an earlier suggestion (543), the potential is of no consequence in the initial stage of the reaction; it may, however, have considerable relevance to the rate of secondary processes. If an air-free aqueous solution of methylene blue ( $E'_0$  = reduction potential at pH 7 =  $-0.011$  v.), bleached by x-ray irradiation, is allowed to stand without admission of air, there is a partial recovery of color. This effect is more marked, and occurs more rapidly, with phenosafranine ( $E'_0$  =  $+0.252$  v.) or neutral red ( $E'_0$  =  $+0.325$  v.) (147). It appears that reoxidation of the leuco dye is occurring by reaction with radicals or oxidation products from the dye or with the molecular yield of hydrogen peroxide. These reactions should occur more rapidly with leuco dyes of more positive reduction potential, and may have led to the conclusion that dyes at this end of the reduction potential scale cannot be completely reduced (543).

In aerated solution the hydroxyl radicals will behave as before, but the hydrogen atoms will probably be converted to  $\text{HO}_2$  (or  $\text{O}_2^-$ ) radicals. Whether or not these radicals will be able to attack the dye appreciably will depend on the type of molecule concerned and on the pH. There is little available evidence on this point. It has recently been reported that the radiation yields of both oxidation and reduction are higher in aerated than in deaerated solutions of methylene blue (568). Such a result, of which no details are yet available, may suggest that the  $\text{O}_2^-$  ion may be acting in both an oxidizing and a reducing capacity.

### 3. Xanthenes

Unlike the other dyes considered, the leuco form of fluorescein is oxidized to fluorescein by irradiation with x-rays,  $\gamma$ -rays, or  $\alpha$ -particles in either aerated or air-free solutions (364). Above a dye concentration of  $5 \times 10^{-4} M$  the yield of oxidation is constant for x-rays [ $G_x(\text{oxidation}) = 3.02$ ]. For  $\alpha$ -particles  $G_\alpha(\text{oxidation}) = 2.25$  at  $7 \times 10^{-4} M$ , but is still increasing with concentration. The investigations were carried out in alkaline solution, so the dye was in the form of the negative ion and reduction might be expected to be more difficult. In fact, the effect of continued irradiation of the fluorescein dye formed led only to irreversible bleaching. A later investigation has shown that whilst the irradiation of alkaline fluorescein in aerated solution gives destruction of both color and fluorescence, irradiation in air-free solution merely destroys the fluorescence (470), so that different parts of the dye ion can be attacked. With eosin under similar conditions a deaerated solution yielded a red product which was partly reoxidizable in air to eosin (471).

### 4. Other dyes

The behavior of the sodium or potassium salts of indigosulfonates under x-ray irradiation does not conform to the usual pattern, in that the yield of bleaching in aerated solution is appreciably higher than that in air-free solutions (147, 446). It has in fact been claimed that the disulfonate is unaffected by irradiation in air-free solution at pH 1.15 (446). This is not the case at pH  $\sim 4$  (147, 543), but the yield is low and there is little reduction. On the other hand there is a very

high yield of bleaching in aerated solution at pH 1.15 ( $G_x = 14.7$  (446)). It seems clear that in this case either the  $\text{HO}_2$  radical is effective or a radical initially formed by OH attack is particularly prone to degradative reaction with oxygen. As might be expected, oxidation occurs at the central  $\text{C}=\text{C}$  double bond, as shown by the fact that the products include isatin-5-sulfonic acid (446). The rate of bleaching of chlorphenol red is also higher in aerated than in deaerated solution (616). Possibly in this case reduction of the negative dye ion is difficult (compare fluorescein above).

Erioglaucine, which is a triphenylmethane dye, gives the same bleaching yield, and spectroscopically the same products, when irradiated in aerated or air-free solution (147). Other triphenylmethane dyes—fuchsin (137), brilliant green (150), and malachite green (71)—also give good bleaching yields in aerated solution. On the other hand, certain dyes of the nitro (Martius yellow) and nitroso (gambine R and fast green O) classes seem quite resistant to irradiation in aerated solution (137), as are also methyl orange (137) (a monoazo dye) and congo red (a disazo dye) (476, 496). The bleaching yields of the pyrazolone dye tartrazine in aerated aqueous solution under irradiation with electrons have been found to be dependent on the dose rate and concentration, even up to  $3 \times 10^{-3} M$  (71). Similar results were found for gentian violet, amaranth, malachite green, brilliant green, aniline yellow, eosin, and methylene blue, in marked contrast to the lack of dependence of yield on concentration down to  $10^{-6} M$  for air-free methylene blue solutions.

Two dyes, resazurin and triphenyltetrazolium chloride, are reduced by irradiation in aerated solution. The case of resazurin is not surprising, since the first step is the *irreversible* reduction of the unstable oxazone to the red azine dye resofurin (260). In such a case even the OH radical may act in a reducing capacity. Subsequently the resofurin is bleached, probably by an irreversible oxidation process. The reduction of triphenyltetrazolium chloride in aerated solution with  $\alpha$ -particle or x-ray irradiation (255) is more difficult to understand, but the fact that the reduction is again an irreversible process (to insoluble formazan) may be important (314).

#### B. AQUEOUS SOLUTIONS WITH OTHER SUBSTANCES PRESENT

Substances which are themselves oxidized by irradiation in aqueous solution have been found to protect dyes against bleaching in aerated solution. Into this category fall the following: acetone (137, 577, 579); sucrose and phenol (577, 579); malonic acid, cystine, succinic acid, and fumaric acid (246); quinone, hydroquinone, glucose, and glycerol (549); formaldehyde, galactose, and azulin ( $\text{C}_{15}\text{H}_{18}$ ) (445); ethanol (445, 577, 579); and thiourea (171). Carbon dioxide, which is not itself oxidized, also protects against bleaching (445, 567, 568). The protection afforded by gelatin and agar is in some doubt (171), but gelatin appears to protect methylene blue, as shown by a decreased bleaching yield (189, 246). Calcium chloride had no effect on the bleaching of methylene blue (577, 579), but sodium chloride was found to inhibit it (246).

The same type of substance tends to *increase* the rate of bleaching in air-free solutions, presumably by removing OH radicals, possibly replacing them with

reducing organic free radicals and certainly preventing their recombination with hydrogen atoms. Thus increased reduction yields have been observed on adding glucose or albumin (543), sodium benzoate (187, 189, 568), ethanol (568, 569), hydrogen (147, 568), or carbon monoxide (147). Thiourea (171) and carbon dioxide (568) *inhibit* bleaching of methylene blue both in aerated and in air-free solution. Calcium chloride slowed down the rate of dye bleaching in air-free solution (543).

### C. NON-AQUEOUS SOLUTIONS

There have been far fewer investigations in this category. Methylene blue (260, 477, 478, 635), toluidine blue, thionine, azur blue, and Nile blue (478) have all been bleached by irradiation in aerated glycerol solution. Moreover it was possible to restore the dye color by subsequent aeration, indicating that the reaction was a reduction. Janus green, which has a much more positive reduction potential than any of the above, was not reversibly bleached in this way (478), probably because at this reduction potential the radicals from the glycerol were capable of reoxidizing the leuco form first produced.

Air-free solutions of dyes in methyl, ethyl, and amyl alcohols were reduced at the same rate as in air-free aqueous solutions (543). Methylene blue was also bleached with some reduction in *aerated* methyl alcohol solution (260). The reduction yield was low, probably owing to the ease of diffusion of oxygen into the system. At a much lower dose rate other observers found no effect of x-ray irradiation on methylene blue in ethanol, using doses up to 10,000 r (246). With fluorescein in alcohol, in the absence of air, no effect was observed up to 150,000 r (478).

An earlier suggestion that the radiation reduction of dyes is achieved by direct electron capture (543), as opposed to the action of hydrogen atoms, receives some support from the fact that reductions can be achieved in chloroform (543) or carbon tetrachloride (189) and in solid solution in polymethyl methacrylate (190). The possibility of other radicals acting as intermediaries is not ruled out, but paramagnetic resonance measurements on the irradiated dye-plastic system indicated that electrons were trapped, partly by the dye and partly by the plastic (523). There is some theoretical backing for expecting electrons to play a direct part in such cases (481, 619), and there is independent evidence for the possible existence of solvated electrons in rigid solutions (385), but as yet there is no clear experimental result which proves whether the reduction of dyes is caused by electron capture or by an indirect effect on the solvent.

## VI. SUBSTANCES OF BIOCHEMICAL INTEREST

### A. STEROIDS

#### 1. General

The application of paper chromatography and other techniques to identify the actual products has recently provided a valuable approach to the radiation chemistry of steroids. Oxidized, reduced, or acetylated products have been obtained, according to the conditions. The products of x-ray irradiation are listed in table 12.

TABLE 12  
The products of the irradiation of sterols

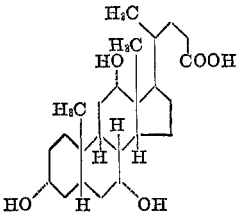
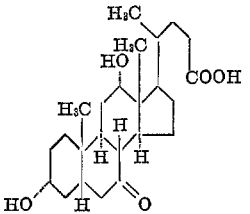
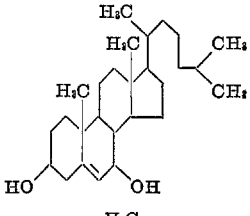
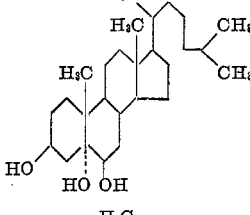
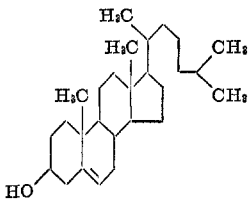
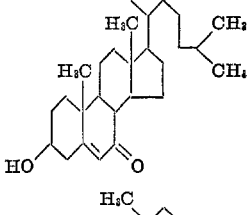
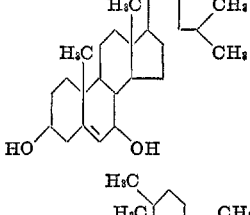
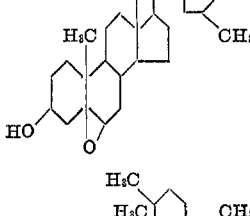
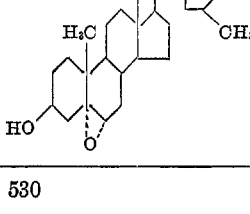
Starting Material	Solvent	Products Identified	Yield	Reference
	Water, saturated with air		per cent 7	(342)
	Methanol		4.5 of mixture	(145)
				
	Acetone or dioxane		5	
			7 (acetone) 4 (dioxane)	(145)
			4 (dioxane)	
			23 of mixture, acetone 3 (dioxane)	

TABLE 12—Continued

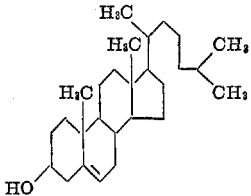
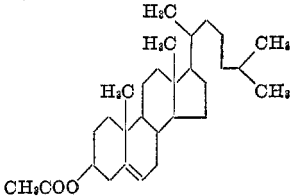
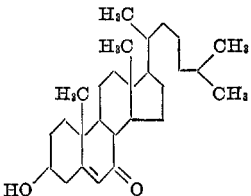
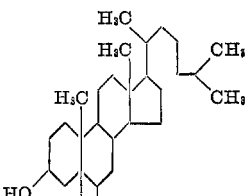
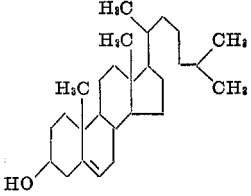
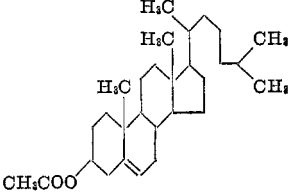
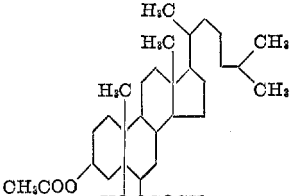
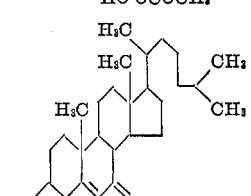
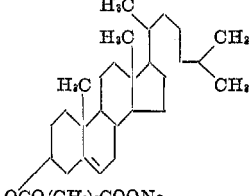
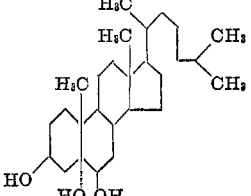
Starting Material	Solvent	Products Identified	Yield	Reference
	Aqueous acetic acid, saturated with air		per cent 4.5	(341)
			17.5	
			27.5	
	Glacial acetic acid, air-free		7	(341)
			4	
			7	
 $\text{OCO}(\text{CH}_2)_2\text{COONa}$	Water, saturated with air		19	(341)

TABLE 12—Continued

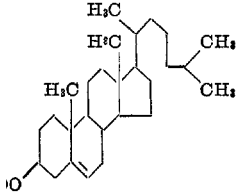
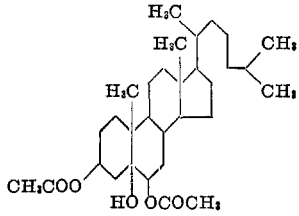
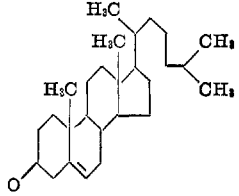
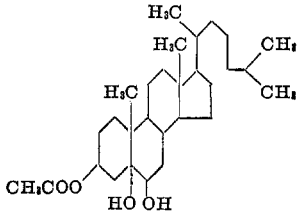
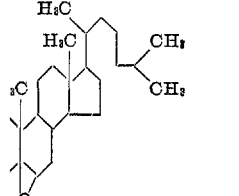
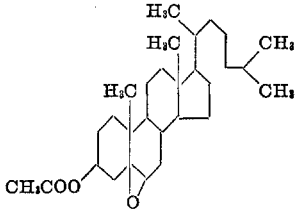
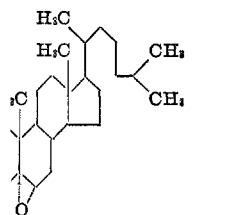
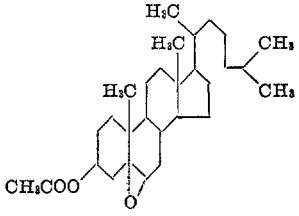
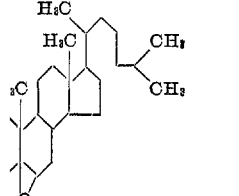
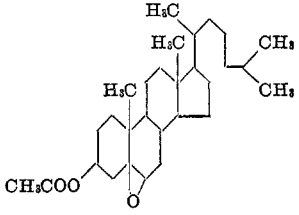
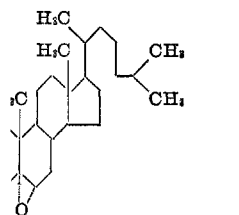
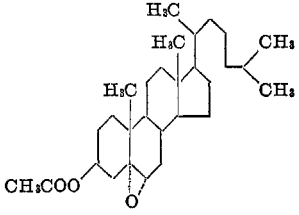
Starting Material	Solvent	Products Identified	Yield	Reference
	Aqueous acetic acid, saturated with air		per cent 32	(341)
	Acetic anhydride		48	
	Aqueous acetic acid; products were identified after acetylation		21 of mixture	(145)
				
	Aqueous acetic acid; products were identified after acetylation		19	(145)
			14	(145)

TABLE 12—Continued

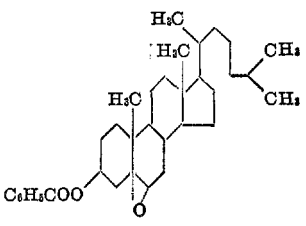
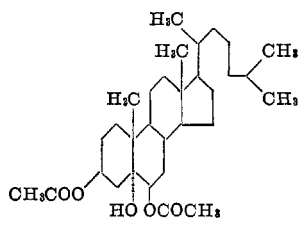
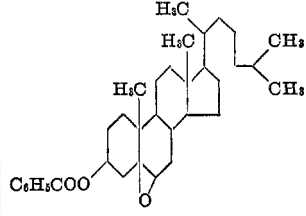
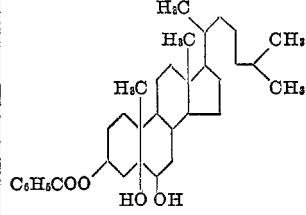
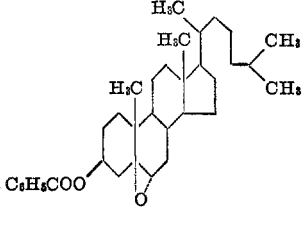
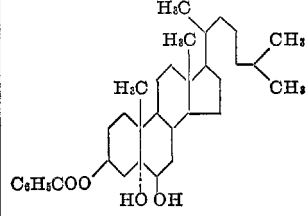
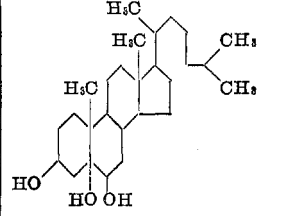
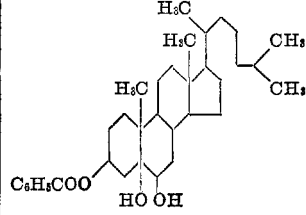
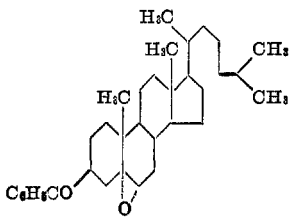
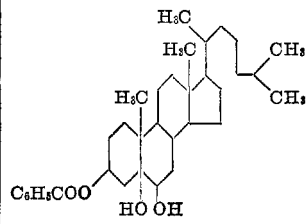

Starting Material	Solvent	Products Identified	Yield <i>per cent</i>	Refer- ence
	Methanol		44	(145)
				
				
	Acetone		9	(145)
				
			1	
	Dioxane		6	(145)
				

TABLE 12—*Continued*

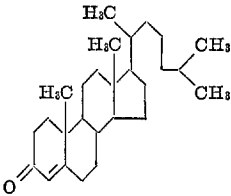
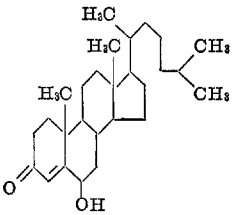
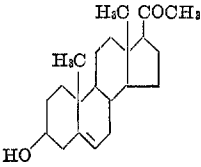
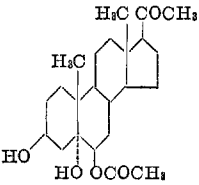
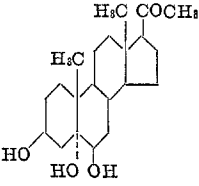
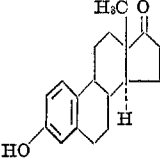
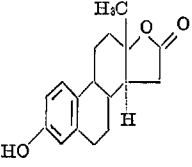
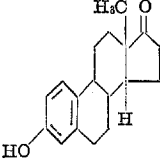
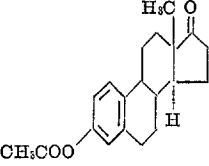
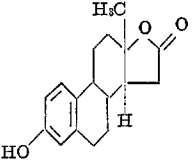
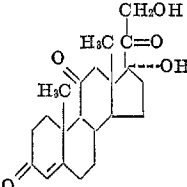
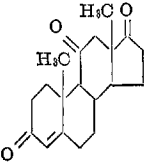
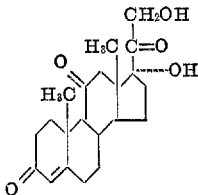
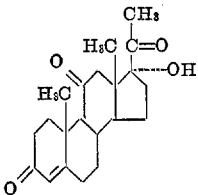
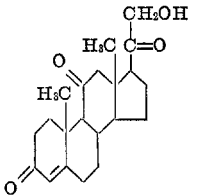
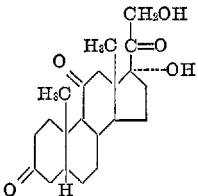
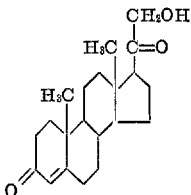
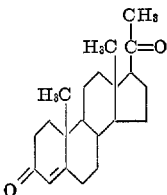
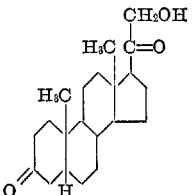
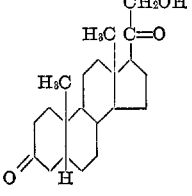
Starting Material	Solvent	Products Identified	Yield	Reference
	Methanol		<i>per cent</i> 4	(145)
	Aqueous acetic acid, saturated with air		18	(341)
			25	
	Aqueous sodium hydroxide		2	(343)
	Aqueous acetic acid		34	(343)
			1	
	Water, saturated with air			(10)



TABLE 12—*Concluded*

Starting Material	Solvent	Products Identified	Yield <i>per cent</i>	Refer- ence
	Water, air-free			(10)
				
				
	Water, air-free			(10)
				
				

It can be seen from table 12 that reduced products appear when sterols are irradiated in oxygen-free aqueous solution, but oxidized products are obtained from air-saturated aqueous solutions and from all the organic solutions tested. The results of irradiation in acetic acid are particularly interesting. The formation of cholesteryl acetate, for example, reveals that ionizing radiations are capable of causing acetylation as well as oxidation in this solvent. The specificity of attack should also be noted. Although the sterol molecules offer a large number of sites of possible attack, the products actually isolated show that attack is

restricted to certain sites, and that in some cases quite good percentage yields are obtained. It has been pointed out that the irradiation products often do not differ from substances which have been isolated from normal biological sources (621).

That the reaction mechanism may be a free-radical one is suggested by the fact that the effect of x-rays on steroids can in some cases be simulated with Fenton's reagent (140). Attempts have been made to suggest detailed reaction mechanisms (341), but these must still be regarded as speculative. It is important to note that unstable organic peroxides have been detected after irradiation of air-saturated aqueous solutions of cortisone (10), so that the presence of peroxides should be suspected in other cases too. Although peroxides are too unstable to be isolated as final products, their presence has important consequences for the reaction mechanism.

## 2. Cholesterol

Besides the work on cholesterol summarized in table 12 there is much earlier work concerned with its "destruction" as measured by the Liebermann test. It was at first claimed that chloroform and benzene solutions were equally readily attacked (505, 506) but later workers, although agreeing that destruction occurs in chloroform, could not confirm the result with benzene (24, 62, 193, 297, 405, 576). There is one claim that ethanol solutions are attacked (500), but this has been denied (24, 63, 405). The most reactive solvents appear to be chloroform and carbon tetrachloride, with bromoform less effective in spite of its greater absorption of radiation (193). It should be noted that chloroform and carbon tetrachloride themselves are highly radiosensitive (see page 488) especially when dissolved oxygen is present, as in the work under discussion. The product or products of irradiating cholesterol in chloroform solutions have not been identified, but the cholesterol appears to have been chlorinated (297) to give a dark-colored wax or oil (62, 297, 499, 500, 506).

Solvents in which cholesterol is little affected include petroleum ether, benzene, toluene, chlorobenzene, ethanol, acetone, ethyl butyrate, and carbon disulfide (24, 193, 405). The more recent work with cholesterol (table 12) was not under comparable conditions.

Solid cholesterol shows little percentage change on irradiation with low doses (506), although the energy yield for decomposition is quite high, being  $-G_{\epsilon\text{- or } \gamma\text{-}}$  (cholesterol) = 3-5 (609). A gas is evolved on  $\alpha$ -particle irradiation, consisting mainly of hydrogen (72). Impure cholesterol gives an antirachitic substance on irradiation with cathode rays, but pure cholesterol does not (349, 350). The antirachitic substance does not appear when cholesterol is irradiated in chloroform solution (581). Ergosterol when irradiated with cathode rays or the radiation from radon gives an antirachitic substance like that produced by ultraviolet light (298, 351, 447). The antirachitic substance itself is destroyed on further irradiation (448, 550).

## B. AMINO ACIDS

## 1. General

With few exceptions, the characteristic reaction of amino acids on irradiation is deamination. The reaction, which is usually carried out in aqueous solution, is not an easy one to understand in detail, for the yield is highly dependent on the conditions of the irradiation. Thus, glycine (173, 176, 177, 574) and serine (174) give yields of ammonia which rise with concentration. The yield from alanine is especially concentration-dependent, that from 1 *M* alanine being twenty times that from *M*/10 alanine (394). Other variables are the pH, which affects the yield in rather a complex manner (316, 574), and the presence of oxygen, which does not affect the yield of ammonia from glycine (176, 574) but decreases the yield from serine (574). The dose given also seems to be important, for using very low doses it has been found that oxygen *increases* the amount of deamination of serine and most other amino acids, and that glycine does not appear to be deaminated at all (34).

In view of the unusually complicated influence of the irradiation conditions it is not very profitable to compare the yields from different amino acids. Those which give ammonia when irradiated in aqueous solution include glycine, alanine,  $\alpha$ -aminoisobutyric acid, valine, leucine, serine, lysine, glutamic acid, asparagine, aspartic acid, phenylalanine, tyrosine, cystine, methionine, histidine, arginine, and tryptophan (9, 50, 176, 394, 571, 578). As is usual for reactions in aqueous solution, the yield from the irradiation of glycine with  $\alpha$ -particles is less than that for less densely ionizing radiations (177). Cysteine is the only amino acid examined which is not deaminated (175). All the peptides, acylamino acids, and acylpeptides that have been examined give ammonia, whether amino groups are present or not (9, 176), but proline and guanidine give no ammonia, and urea gives very little (176).

Hydroxylamine is a general product of the irradiation of amino acids and other amino compounds in aqueous solution, and it has been shown not to originate from a secondary action on ammonia (529).

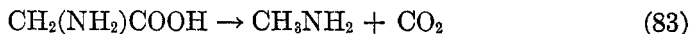
Organic peroxides have been detected after irradiation of amino acids in aqueous solutions containing dissolved oxygen (358).

## 2. Glycine

An extensive analysis has been made of the products of the x-ray irradiation of air-free solutions of glycine (418). By extrapolating yields to zero dose, elimination of the complication of a further reaction on the products was attempted. The most important primary reactions appear to be (in decreasing order of importance) oxidative deamination to glyoxalic acid, reductive deamination to acetic acid, and oxidative deamination accompanied by decarboxylation to give formaldehyde.



In concentrated solutions, what appears to be a direct action of the radiation decomposes glycine into methylamine and carbon dioxide.



In agreement with this, methylamine and carbon dioxide were found to be the two products isolated in greatest yield from dry glycine bombarded with electrons (609). Ammonia, acetic acid, a dicarboxylic acid, and hydrogen are also formed from dry glycine, but a detailed study has not yet been made (72, 609).

Electrons give the same products as x-rays from aqueous solutions of glycine (419). In the presence of dissolved oxygen it was discovered that electrons produce hydrogen peroxide, and this reacts slowly with glyoxalic acid after the irradiation has stopped, to give formic acid (623). Hydrogen peroxide causes only a slight amount of deamination (177).

### 3. Alanine

The equations given above for glycine also apply for alanine, the corresponding products—pyruvic acid, propionic acid, acetaldehyde, and ethylamine—all having been isolated (548). No inversion of L-alanine to D-alanine could be detected. In the presence of dissolved oxygen the yield of pyruvic acid is enhanced compared with that of acetaldehyde (316), and acetic and formic acids appear (548).

### 4. Serine

Serine is deaminated to give predominantly a dialdehyde (glyoxal) in oxygen-saturated solutions and a monoaldehyde (glycolaldehyde) in hydrogen-saturated solutions (574). A complete analysis of the products has not yet been made.

### 5. Tyrosine

Tyrosine, like other aromatic substances, is hydroxylated in aqueous solution. 3,4-Dihydroxyphenylalanine is produced, but there is little or no 2,4-dihydroxyphenylalanine. Substances of higher molecular weight are produced by irradiating tyrosine, phenylalanine, and tryptophan (397), and as these appear to be produced only from aromatic amino acids, it is possible that they may be dimers of the biphenyl type. Deamination of tyrosine occurs as well as attack on the nucleus, but the products (other than ammonia) have not been isolated. There is little or no decarboxylation to tyramine (514).

Hydroxylation of the benzene ring explains why tyrosine "decomposition" as measured with Folin's reagent (576) is less than that found by the more reliable microbiological technique (491). Using Folin's reagent it was found that "decomposition" is, as usual in aqueous solution, less ready with  $\alpha$ -particles than with x-rays (465, 636).

Tyrosine and dihydroxyphenylalanine, as well as other substances commonly used as substrates for peroxidases, have been irradiated in aqueous solution containing oxygen to demonstrate that the effect of ionizing radiations is often

similar to that of peroxidases (395). The results are discussed under "Aromatic Compounds" (page 515).

### 6. *Histidine*

When irradiated with x-rays, cathode rays, or ultraviolet light, histidine gives a substance with histamine-like properties (51, 205). The product of the ultraviolet irradiation of histidine was later proved chemically to be in fact histamine (301, 302) in spite of an earlier suggestion that it was not (598). Histidine is also deaminated, and ring fission probably occurs (57).

### 7. *Miscellaneous amino acids*

Spectroscopic measurements have been made on x-ray irradiated asparagine, aspartic acid (49, 50), proline, and oxypoline (48), but little can be said about the nature of the products. Arginine has been shown to give urea (394). Leucine gives isovaleraldehyde (52).

Cysteine and cystine are dealt with under thiols (see below).

From some points of view it is of interest to know the amount of starting material decomposed rather than the products obtained. Such information has been given for aqueous solutions of amino acids (491, 494), and for the decomposition of  $C^{14}$ -labelled compounds in the dry state under the influence of their own  $\beta$ -particles (367, 607, 608).

## C. THIOLS AND DISULFIDES

It was noted in the previous section (page 537) that cysteine is the only amino acid not deaminated by radiation. This is due to the presence of the thiol group, which competes successfully for the free radicals and other reactive species present in irradiated water.

### 1. *The oxidation of thiols*

The readiness with which thiols are affected by radiation is mainly due to the ease with which they are oxidized. The thiols shown to have been oxidized by ionizing radiations are 1,3-propanedithiol (39), 2,3-dimercapto-1-propanol (BAL) (39), *N*-phenylaminopropanedithiol (39), cysteine (588, 622), and glutathione (39, 267, 272, 631). The main product of oxidation has been shown to be the corresponding disulfide (622). Other non-volatile products include cysteic acid, alanine, serine, and possibly pyruvic acid (541).

As might be expected, there is a higher oxidation yield with dissolved oxygen present (39, 588); an increase in pH, within limits, is also favorable to oxidation (39, 622). The yield increases with thiol concentration (588, 622), and for a 0.051 *M* solution as many as 74 molecules of cystine can be oxidized per 100 e.v. absorbed (588). Such high yields are suggestive of a chain reaction.

The amount of hydrogen peroxide formed in irradiated cysteine solutions is greater than that from pure water, except in alkaline solution (358, 622). Part of the oxidation of thiols by radiation appears to be due to slow reaction with the

hydrogen peroxide, for in some cases the presence of catalase during irradiation was found to decrease the yield by about one-quarter (39).

### *2. Minor reactions*

A minor product of irradiating aqueous solutions of thiols is hydrogen sulfide. As for oxidation, the yield increases with concentration (175). There is disagreement on whether oxygen affects the yield or not (175, 622).

Thiourea has been reported to give sulfur, the yield rising to more than  $G = 9$  in concentrated solutions (173).

A study of a different kind has been made on the effect of x-rays on the chemical reaction between glutathione and 1,4-naphthoquinone. Degradation of the starting materials and of the intermediate and final products can occur, but with small doses the rate of the normal reaction can be influenced in a rather complicated way (244).

### *3. Disulfides*

Cystine in aqueous solution is attacked by x-rays and probably gives cystine disulfoxide (512). Some deamination occurs, but the formation of hydrogen sulfide as a primary product is doubtful (175, 394, 491, 512). Reduction of disulfides to thiols is not generally observed (39, 512), but there is one claim that this occurs for cystine solutions saturated with molecular hydrogen (588).

## D. PROTEINS

Much of the early work on the radiation chemistry of proteins was reviewed in 1936 (22). The effects produced by ultraviolet light and ionizing radiations seemed at the time to be so similar that it was hardly necessary to differentiate between the two. Since then the concept of indirect action has arisen, and indeed it was in work with aqueous solutions of enzymes that it first became apparent that indirect action is important in the action of ionizing radiations on substances of biological interest (166, 168).

### *1. Direct action*

The action of ionizing radiations on proteins in aqueous solution is almost entirely due to the indirect effect, but there is one field—the irradiation of dry enzymes and proteins—where the direct effect is important. Results are interpreted in terms of the target theory, which in its simple form states that a single ionization within a molecule will be sufficient to inactivate it (363). The theory has been found to be true for several enzymes, proteins, and other substances, including pepsin, trypsin, invertase, and chymotrypsin (483). An important application of the target theory to enzymes and proteins is the determination of molecular size by measuring the inactivation produced by known amounts of radiation. Larger molecules require smaller doses to produce the same amount of inactivation. An attraction of the method is that although dry samples are required they need not be pure.

It is important to note that the direct effect, requiring ideally one ionization

per molecule for inactivation (i.e.,  $G = 3$  molecules inactivated per 100 e.v. absorbed in the protein), is nearly always more efficient than the indirect effect (where one considers the energy absorbed in the whole solution). The only exceptions are the sulfhydryl enzymes (33). The point has been established for pepsin by direct comparison (14, 52). In dilute solution, of course, the amount of energy absorbed directly in the protein is so small that, in spite of its efficiency, the direct effect is not the principal cause of reaction.

The whole subject of the irradiation of dry enzymes and proteins and of other substances has recently been reviewed elsewhere (483).

## 2. *The inactivation of enzymes in aqueous solution*

### (a) The effect of linear energy transfer

With very few exceptions, all work on aqueous solutions of enzymes and proteins has been with x-rays,  $\gamma$ -rays,  $\beta$ -particles, and fast electrons, i.e., with the less densely ionizing radiations. One of the exceptions is the action of  $\alpha$ -particles on carboxypeptidase.

The yield for the destruction of carboxypeptidase by  $\alpha$ -particles was found to be about 0.03 molecule destroyed per 100 e.v., i.e., about one-twentieth of the x-ray yield. From a very detailed study of the reaction it was concluded that the whole of the action of the  $\alpha$ -particles can be attributed to the  $\delta$ -rays emanating from the track (180). The ions and radicals in the track itself do not affect the enzyme but give hydrogen peroxide with the same yield as from pure water (178).

### (b) The effect of enzyme concentration

In work with aqueous carboxypeptidase and polyphenoloxidase it was found that over a wide range of concentrations the actual amount of enzyme destroyed was proportional only to the energy absorbed by the solution and was independent of concentration (166). This is of course the result expected on the basis of simple indirect action. However, for pepsin the amount of enzyme inactivated by radiation increases slowly with concentration in the range over which carboxypeptidase inactivation is constant (i.e., above 0.2 mg. protein per milliliter) (52). Below this range, as for carboxypeptidase, the yield falls markedly (464). For trypsin the yield increases even more markedly with concentration, up to the highest concentrations studied (7 mg./ml.) (338, 339). Such behavior is not unique in radiation chemistry (e.g., see amino acids, page 537) and does not necessarily indicate that the effect of radiation is not indirect. The effect may arise from a complicated reaction mechanism.

### (c) The effect of other irradiation conditions

The yield of pepsin (313) and trypsin (422) inactivation is not strongly temperature-dependent, but frozen solutions of enzymes are less affected (52, 58, 311).

Trypsin has been found to be most resistant to radiation inactivation at pH 6, in contrast to thermal inactivation for which the maximum stability is at pH 2.3 (340). A feature of trypsin inactivation which is difficult to explain except

by some unique property of the protein molecule is that fresh solutions are more sensitive than "aged" solutions to inactivation both by radiation and by heat (513).

Experiments have been carried out on the inactivation of surface films of pepsin and pepsin-albumin (420, 421, 559) which may give information about the lifetime of free radicals and the way in which the enzyme-substrate film is organized. The results are rather difficult to understand, and a complete interpretation cannot yet be given.

#### (d) The after-effect

It has been known for about forty years that ionizing radiation renders protein more easily coagulable by heat (219). The physical chemistry of the process has received further study (238, 239, 240), and it has been shown that irradiation accelerates the process of heat coagulation without altering its qualitative features (239). When the protein is an enzyme, the phenomenon manifests itself in a slow temperature-dependent decrease in activity after irradiation has stopped (15, 16, 65, 340, 422, 431). This interesting result shows that the enzyme has retained its activity even though it has been altered in such a way as to become thermally unstable.

The after-effect is quantitatively very important, several times as much activity being lost in this way as in the immediate effect of irradiation. In the case of pepsin (15, 16), whereas the immediate effect of radiation is independent of the presence of dissolved oxygen, the after-effect is greater when the solution contains dissolved oxygen during irradiation. The presence of oxygen *after* irradiation is unimportant, and hydrogen peroxide is not responsible for the after-effect.

#### (e) The mechanism of inactivation

An attempt has been made to discover which active species is responsible for the inactivation of ribonuclease by x-rays (299, 300). Hydrogen peroxide does not seem to be responsible, for three reasons. Firstly, added hydrogen peroxide did not inactivate ribonuclease. Secondly, the radiation inactivation was the same in aerated or in air-free solutions. Thirdly, catalase did not protect the enzyme from inactivation by radiation. In the latter case one has to consider whether the catalase may be acting as a peroxidase, instead of merely decomposing the hydrogen peroxide. The evidence taken as a whole, however, appears to be conclusive.

Further experiments on ribonuclease were performed with free hydroxyl radicals generated independently of radiation (300), and it was found that Fenton's reagent, photoactivated hydrogen peroxide, and photoactivated ferric ions would all cause inactivation. It is therefore clear that free hydroxyl radicals can inactivate ribonuclease, and that the action of radiation on aqueous solutions of the enzyme can be ascribed to the action of these radicals.

#### (f) The protective effect

An important consequence of the concept of indirect action in aqueous solution is that the free radicals produced from water are able to react with *any* dissolved



TABLE 13  
*Relative protective powers against irradiation (170)*

Substance	Relative Protective Power per $\mu\text{g.}$ (Carboxypeptidase as Indicator)	Substance	Relative Protective Power per $\mu\text{g.}$ (Carboxypeptidase as Indicator)
Tobacco mosaic virus.....	30	Formate.....	320
Bushy stunt virus.....	20	Oxalate.....	1.5
Crystalline egg albumin.....	17	Thiourea.....	1120
Denatured egg albumin.....	20	Urea.....	0.5
Alanine.....	39	Alloxan.....	13
Glucose.....	34	Mesoxalate.....	7

substance. Therefore if two solutes are present, it is unlikely in general that one of them will capture all the radicals. The protection of one substance by another is known as the protective effect. It was first observed for biological materials in the irradiation of flavin adenine dinucleotide (172, 293), when a number of amino acids, nucleic acids, carbohydrates, and other substances were shown to protect the nucleotide to some extent. By the same mechanism the irradiation product frequently protects the starting material from further attack (181). In general, impurities will act as protective agents, so that pure substances are more affected by radiation than impure substances. The protective effect is now so well established that it is unnecessary here to tabulate the enormous number of examples in the radiation chemistry of enzymes and other substances. Some idea of the variation in protective power of different substances can be seen from table 13.

It is sometimes found that a protective substance becomes relatively less effective when it is present in high concentration (170, 172, 179). This effect has been called "the phenomenon of the changing quotient." The explanation is that the free radicals produced from water by radiation do not always react with protective substances to give a final stable product, but usually give another free radical. These free radicals may or may not react with the protected substance to cause inactivation. It is therefore apparent that highly complex behavior is possible, and a simple characterization of the "protective power" of a substance is not in general to be expected.

(g) Use of the protective effect in determining reaction mechanism

It might be expected that the nature of the most efficient protective substances could give information about the active species responsible for enzyme inactivation. An early attempt to do this for catalase indicated that whereas oxidized substances such as cystine or oxidized glutathione would protect catalase, the reduced substances cysteine and glutathione would cause its inactivation to be increased (226). This work supported the idea that hydrogen atoms are the inactivating agents. However, later experimenters failed to confirm the earlier results and showed that both cysteine and cystine would protect catalase (182, 183). The earlier workers may not have taken into account the thermal inactivation of catalase by cysteine.

The protection of catalase by potassium iodide seems to indicate that inactiva-

tion is by hydroxyl radicals (226, 586), since the iodide ion would be likely to react with hydroxyl radicals in the following way:



The conclusion that hydrogen atoms are *not* responsible receives some confirmation from results obtained with hydrogen atoms, generated either by the action of ultraviolet light on sodium iodide or by diffusion of electrolytically produced hydrogen atoms through palladium (586). Catalase could not be inactivated by either method.

The radiation chemistry of catalase is in many ways difficult to understand (224, 225). Hydrogen protects under some circumstances, but not under others. The dose rate is important, radiation delivered at the lower rates being more effective. There are also puzzling after-effects, the activity sometimes increasing and sometimes decreasing after irradiation has stopped.

### *3. Sensitive groups in the protein*

It was mentioned above that enzymes containing essential —SH groups are more radiosensitive than others. An exact comparison of yields cannot be made because of the influence of the irradiation conditions, different for each enzyme, but the general conclusion is certain. An important reason is the readiness with which thiols are oxidized by radiation, and in agreement it has been found that for numerous sulfhydryl enzymes (phosphoglyceraldehyde dehydrogenase, adenosine triphosphatase, succinoxidase, urease, and alcohol dehydrogenase) glutathione, added after irradiation, will restore part or all of the lost activity (36, 37, 42). These effects must be due, at least partly, to the radiation-induced oxidation of thiol groups to disulfides. Not many other purely chemical changes have been determined for irradiated proteins, but ammonia has been shown to be liberated (176, 346) and organic peroxides have been detected (358).

### *4. Changes in physicochemical properties of proteins*

#### *(a) Electrophoretic changes*

A change in electrophoretic mobility would be expected from the chemical results described above, especially from the fact that ammonia is liberated. That the capacity of proteins to bind dyes and inorganic ions is altered by radiation (34, 52) would also lead to this expectation.

In fact, the electrophoretic properties can change, and with very small doses (about 100 r) (160). With increasing dose the mobility first decreases and then increases. A full explanation of the results must take into account the changes in stability of inorganic colloids on irradiation, it being found in general that positively charged colloids are coagulated or their stability is diminished, whereas negatively charged colloids are hardly affected at all (266). It does not seem possible at present to give any valid explanation of these phenomena.

With larger doses it is found that changes in electrophoretic pattern provide a rather insensitive index of the effect of radiation on proteins (35, 38, 106). There is one interesting study which has shown that whereas purified proteins appear

to be unaffected by this criterion, mixtures give a product with different electrophoretic properties from the original. These results suggest a radiation-induced intermolecular reaction between proteins of different type (344).

#### (b) Changes in absorption spectrum

It has been known for about twenty-five years that the ultraviolet absorption spectra of many proteins suffer a rather unspecific increase in optical density upon irradiation of their aqueous solutions (564, 565, 566). This result has been confirmed recently for bovine serum albumin, serum globulin, and egg albumin (38, 41, 106), and it is now believed that where this happens the changes may be due to an attack on the tyrosine component, similar to that occurring on tyrosine itself (38). In cases where the ratio of tryptophan to tyrosine is greater than 1, the absorption spectrum shows a *decrease* on irradiation, especially near 280  $m\mu$ . This seems to be due to an attack on the tryptophan component, for tryptophan itself shows a decrease in absorption spectrum in this region when irradiated (34).

#### (c) Changes in molecular weight

Two of the observations mentioned above lead to the expectation that proteins should increase in molecular weight on irradiation in solution. Firstly, the formation of disulfides could result in protein dimers being formed, and secondly, if tyrosine is attacked, one might expect that some proportion of the protein molecules would be linked together by a diphenyl linkage, as found after the irradiation of aqueous benzene.

Measurements of viscosity and ultracentrifuge pattern show that this expectation is fulfilled. The viscosity of fibrinogen (352, 553) and bovine serum albumin solutions (35, 38, 106) increases on irradiation with moderate doses, and the ultracentrifuge pattern shows that components of higher molecular weight are present. With fibrinogen, components of lower molecular weight are present as well. The molecular weights of gelatin (346) and salmine (105) do not increase on irradiation. For salmine at least this is not surprising, for neither sulfhydryl nor aromatic groups are present.

### 5. *The inactivation of toxins*

Toxins have been shown to be inactivated on irradiation of their aqueous solutions. The presence of oxygen increases the rate (400). The usual protection effects have been observed (103, 202, 207).

## E. VITAMINS, COENZYMES, AND RESPIRATORY PROTEINS

### 1. *General*

The irradiation of vitamins is of current technical interest in connection with the radiation sterilization of food and also from a medical point of view. Detailed information on the pure chemicals is, however, often surprisingly scanty. For example, little is known about the radiation chemistry of  $\beta$ -carotene (107, 259), riboflavin (493), flavin adenine dinucleotide (167, 179), pyridoxine (337), or vitamin B<sub>12</sub> (415) except that these substances can be destroyed when irradiated in solution.

## 2. Nicotinic acid

Rather more information is available about nicotinic acid and its derivatives. It was demonstrated by a radioactive tracer technique that when nicotinic acid dissolved in air-saturated water is irradiated, decarboxylation is the first reaction to take place, and that ring splitting does not occur until a later stage (261).

Nicotinic acid is also destroyed when irradiated in air-saturated aqueous solution containing ethanol. When an aqueous solution of ascorbic acid and oxalic acid is added, the destruction is increased (492, 493). Ascorbic acid itself, which is also radiosensitive (see page 547), is less so in the system with nicotinamide than when dissolved in aqueous oxalic acid. The chemical reactions in a system as complex as this would be exceedingly difficult to elucidate.

An aqueous solution of nicotinamide is less affected when irradiated frozen at  $-35^{\circ}\text{C}$ . than in the liquid phase at  $18^{\circ}\text{C}$ . (310).

## 3. Coenzyme I

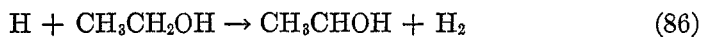
Diphosphopyridine nucleotide, when irradiated in aqueous solution, suffers a very slight attack ( $G = 0.01$ ), as shown by a decrease in optical density at the characteristic absorption peak at  $260\text{ m}\mu$  (32). If, however, ethanol or any of several other substances is present during irradiation, and if oxygen is excluded, then irradiation leads to a quite different result: namely, the formation of a reduced product in good yield ( $G = 6.9$  molecules reduced per 100 e.v. absorbed) (569, 589, 591, 592). There is one experiment suggesting that the product consists partly of the normal dihydrodiphosphopyridine nucleotide (43), but this has recently been interpreted differently (591), and it is now clear from experiments with alcohol and lactic dehydrogenases, and also from the lack of fluorescence, that *none* of the irradiation product is identical with ordinary dihydrodiphosphopyridine nucleotide. Experiments with nicotinamide methochloride and propyl chloride as models suggested at first that the product might be a form of diphosphopyridine nucleotide reduced at a different position in the pyridine ring (568, 569), but it now seems more likely that the product is a dimer (592).

Species that could possibly be responsible for the reduction are atomic hydrogen or free hydroxyethyl radicals formed by the reaction:



With Fenton's reagent and ethanol as a source of radicals, it has been shown that free hydroxyethyl radicals are capable of reducing tetrazolium salts (406). Four pieces of evidence lead to the conclusion that, on irradiation, diphosphopyridine nucleotide is reduced by organic radicals rather than by hydrogen atoms (589, 590, 591, 592). Firstly, no reduced form appears when diphosphopyridine nucleotide is irradiated in the presence of molecular hydrogen, a system in which the concentration of free hydrogen atoms is increased by reaction 48. Secondly, no reduced form appears on irradiation in the presence of sodium benzoate, although the latter would be expected to remove hydroxyl radicals, leaving hydrogen atoms as possible reducing agents. Thirdly, hydrogen atoms diffusing

through a palladium foil, although capable of reducing methylene blue, cannot reduce diphosphopyridine nucleotide. Fourthly, and most convincing, the yield of molecular hydrogen from ethanol solutions containing diphosphopyridine nucleotide [ $G_x(\text{H}_2) = 3.2$ ] is not less than that from ethanol solutions without diphosphopyridine nucleotide, a result that can only be explained if free hydrogen atoms do not cause the reduction but give molecular hydrogen by the reaction:



When dihydrodiphosphopyridine nucleotide is irradiated in air-saturated aqueous solution, it is oxidized to give the normal active form of the coenzyme (43).

#### 4. Thiamine

The activity of thiamine can be destroyed by irradiation in air-saturated aqueous solution (199). This appears to be due to attack at the pyrimidine or thiazole nuclei (201). There is little thiochrome or thiamine disulfide among the products. The effect of radiation on cocarboxylase is similar (201).

#### 5. *p*-Aminobenzoic acid

*p*-Aminobenzoic acid is destroyed by x-rays (414, 604). This is due to decarboxylation, deamination and, as shown by a decrease in ultraviolet absorption, a change in ring structure (158).

#### 6. Ascorbic acid

Ascorbic acid is oxidized by x-rays when irradiated in aqueous solution (13, 17) or in a solution containing oxalic acid (200, 492, 493, 495). Dehydroascorbic acid seems to be the initial product in both systems. On further irradiation still further destruction occurs, but 2,3-diketogulonic acid does not appear to be produced (495). Effects are less in the frozen state (310, 495).

#### 7. Auxin

$\beta$ -Indolylacetic acid has been shown to be sensitive to radiation, whether dissolved in water or in chloroform (555). A related reaction is the decomposition of indole by radiation. From a study using remarkably low doses, in most cases less than 20 r, it was shown that results are not inconsistent with an initial oxidation to indole-5,6-quinone, followed by an oxidative condensation with unchanged indole (11).

#### 8. Cytochrome c

Ferricytochrome c can be reduced to ferrocyanochrome c by irradiation in air-free solution containing sodium benzoate or succinate (432). In air-free solutions in the absence of any added substance, or with hydrogen or ethanol present, there is a different reaction. An autoxidizable product is formed on irradiation, which after reaction with oxygen shows an absorption band at 600 m $\mu$  (357, 432).

Ferrocyanochrome c is oxidized by radiation when irradiated alone in aqueous

solution, and the product reacts with oxygen to give the substance with an absorption band at 600  $m\mu$  (357). Hydrogen peroxide does not appear to be the oxidizing agent, for the prior addition of catalase does not affect the yield. It therefore seems likely that the oxidation is due to hydroxyl radicals (40).

### 9. Hemoglobin

Oxyhemoglobin and hemoglobin are oxidized on irradiation in aqueous solution (243, 293, 294, 357). Methemoglobin is reduced (357). There are also the usual effects on proteins: i.e., immediate denaturation and the formation of a product with decreased thermal stability (240, 243).

When irradiated in the dry state, hemoglobin is not oxidized, but it becomes insoluble and there are other changes (19, 20).

### 10. Hemocyanin

The effect of x-rays on aqueous hemocyanin is to cause aggregation (475). This is due to indirect action, as shown by the protection afforded by other proteins.  $\alpha$ -Particles, however, have been shown to cause splitting of the hemocyanin molecule (78, 587). This occurs equally in solution and in a frozen solution at liquid-air temperature, suggesting that in this case the effect may be a direct one.

## F. POLYSACCHARIDES

All the polysaccharides that have been irradiated have been shown to be degraded.

### 1. Aqueous solutions

When a polysaccharide is irradiated in aqueous solution the viscosity decreases (217, 347, 348, 416, 497, 504, 524). For starch, agar-agar, and gum arabic the formation of reducing substances has been demonstrated and the pH has been shown to decrease (347, 348). Hyaluronic acid exhibits a viscosity after-effect, but the decrease in viscosity after irradiation is less than that during irradiation (416, 497, 524). Very little is known about the mode of action, except that Fenton's reagent, like radiation, produces a viscosity decrease on alginic acid (217), thus implying that hydroxyl radicals could be the effective agents.

### 2. Dry polysaccharides

Rather larger doses are required to affect polysaccharides in the "dry" state (504), but qualitatively the effect is the same (345). Cellulose is degraded on irradiation (127), to give water-soluble products. Reducing sugars appear (360), and the ease of acid hydrolysis increases (519). The results are in quantitative agreement with the occurrence of random decomposition of monomer units, each monomer destroyed leading to one main-chain fracture (131).

The degradation of dextran is accompanied by an increase in branching, and there is also rupture of the glucose rings. Each of these events is accompanied by the production of two reducing end groups (490a).

## G. NUCLEIC ACIDS AND RELATED COMPOUNDS

The principal interest in the radiation chemistry of nucleoproteins and nucleic acids derives from their importance in radiobiology. Almost all of the work has therefore been carried out with aqueous solutions. Very much smaller doses are required to produce changes in solution than in the dry state, showing that the effect is largely indirect (94, 370).

Viruses have been irradiated, both dry and in solution (484), but highly organized substances cannot be considered here.

*1. Dry nucleic acids*

One nucleic acid has been irradiated in the dry state to determine its molecular weight (222). It was found that very much larger doses were needed to destroy its ability to be hydrolyzed by deoxyribonuclease than to destroy its *Pneumococcus*-transforming activity (558). This result recalls the not dissimilar observation on aqueous solutions to the effect that doses which decrease the viscosity hardly affect the hydrolysis by deoxyribonuclease (601, 603).

*2. Solutions of nucleoproteins*

The rigidity of nucleoprotein solutions is decreased on irradiation (209) and continues to decrease after the irradiation has stopped (210). A similar result is the decrease in viscosity of a nucleoprotein solution (562). Cysteine increases the viscosity of an alkaline solution but protects against the decrease observed when the solution is irradiated (216).

A distinction has to be drawn between the anomalous "structural" viscosity of nucleic acid and nucleoproteins, which is dependent on rate of shear and is largely due to interaction between the molecules, and the intrinsic viscosity, which depends on the size and shape of the molecules and is usually less dependent on the rate of shear. The normal spontaneous decrease in the structural viscosity of nucleoprotein solutions is accelerated by radiation, but with sodium chloride added to suppress the structural viscosity, the intrinsic viscosity is found not to decrease with the same doses (54).

Deoxyribonucleoprotein fibers in an aqueous sodium chloride suspension have been irradiated with fast electrons. The complex appears to be split, for soluble deoxyribonucleic acid appears in solution, though soluble protein could not be detected. Nitrogen mustards, which often have the same effect as radiation on nucleic acids, were found not to produce this effect (515).

*3. Changes in viscosity of nucleic acid solutions*

Many workers have studied the radiation-induced decrease in viscosity of deoxyribonucleic acid (562, 617). The structural viscosity decreases on irradiation and goes on decreasing for many hours after the irradiation has stopped (601, 602, 603, 617). Many workers agree that the initial effect is independent of whether dissolved oxygen is present or not (153, 154, 560), but others find that the initial effect is substantially less in the presence of oxygen (184, 185). No explanation for the discrepancy can yet be advanced.

The magnitude of the after-effect is dependent on the experimental condi-

tions. If the viscosity of the irradiated solution is measured directly, i.e., without diluting it first, it is found that there is an after-effect whether it was irradiated in the presence of oxygen or not, the after-effect for air-saturated solutions being about three times as great as for air-free solutions (153, 154, 184). But when the irradiated solutions are diluted to twice their volume before the viscosity is measured, or if sodium chloride is added, no after-effect can be detected unless oxygen was present during irradiation (95, 153, 154, 185). The fact that the after-effect for solutions irradiated oxygen-free can be so easily eliminated suggests that the nucleic acid does not suffer a very profound alteration after the irradiation has stopped. The after-effect in oxygenated solution appears to be more important.

The initial decrease in viscosity is not highly temperature-sensitive, although frozen deoxyribonucleic acid solutions are hardly affected by radiation (370, 583). The after-effect is more sensitive to temperature and is much less at 0°C. than at room temperature (601, 603).

#### *4. Other physicochemical changes in nucleic acid solutions*

The viscosity of nucleic acid solutions could conceivably be decreased either by eliminating the interaction due to hydrogen bonding between the molecules or by degradation to fragments of lower molecular weight. Viscosity changes are, therefore, very difficult to interpret, and it would seem desirable to employ more fundamental techniques. Measurements of streaming birefringence indicate that degradation occurs on irradiation (617). Measurements of sedimentation and diffusion constants of irradiated nucleic acids have also shown that degradation has occurred to give highly disperse fragments (156, 370, 603). The fragments, however, are not dialyzable, indicating a molecular weight above 10,000 (601). These results show that the decrease in viscosity can be satisfactorily explained as being due to degradation.

#### *5. Entities responsible for the viscosity effects*

Work with sources of free radicals other than radiation suggests that free hydroxyl radicals are responsible for the decrease in viscosity of nucleic acid solutions on irradiation. Thus, Fenton's reagent decreases the viscosity of nucleic acid solutions (99, 264, 370), and photoactivated hydrogen peroxide, also a source of free hydroxyl radicals, behaves like radiation in causing the viscosity to decrease both during illumination and afterwards (96, 99, 152, 560). Light-scattering and other studies indicate that the nucleic acid is degraded by this reagent, as by x-rays (560, 561). Hydrogen and palladium black have no effect on nucleic acid, suggesting that hydrogen atoms are probably without effect (560).

Hydrogen peroxide reduces the viscosity of some samples of deoxyribonucleic acid (97) but not of others (94, 264, 601, 603). A possible reason is suggested by the observation that thiourea, ascorbic acid, or cysteine will cause hydrogen peroxide to affect samples of nucleic acid which are insensitive to hydrogen



peroxide alone (155, 370). Possibly the "sensitive" nucleic acids contain impurities capable of the same effect.

It was also found that an "insensitive" nucleic acid became sensitive to added hydrogen peroxide after irradiation (152, 155). This suggests the possibility of the after-effect being due to a slow reaction of radiation-damaged nucleic acid with hydrogen peroxide, to give free hydroxyl radicals which would decrease the viscosity of undamaged nucleic acid. Such an explanation cannot be complete, for three reasons. Firstly, very little hydrogen peroxide is found in irradiated nucleic acid solutions (95, 155, 211). Secondly, cysteamine, cystinamine, or sodium cyanide, good protective agents against the primary effect, cannot inhibit the after-effect when added after irradiation (152). Thirdly, degradation of nucleic acid takes place even after redissolving freeze-dried irradiated material (155). In this case no hydrogen peroxide could be present. Clearly some further explanation of the after-effect is required.

#### *6. Chemical changes in nucleic acid solutions*

Information about both the primary effect and the after-effect can be obtained from studies of the purely chemical changes consequent on irradiation. Early attempts to detect decomposition products such as ammonia, inorganic phosphate, and free bases were unsuccessful, owing to the low doses used (603). However, it is clear that important consequences could be drawn from the existence of even small amounts of decomposition products. It is therefore justifiable to use large doses to obtain enough product for analysis, even though such doses are far in excess of those required to cause viscosity changes. It is unlikely that the purely chemical reactions taking place will be different once the nucleic acid has lost its high viscosity. Additional justification for the use of large doses has been found in the fact that it has been possible to repeat with low doses ( $10^4$ – $10^5$  r) some of the results obtained with higher doses ( $10^6$ – $10^7$  r) (528, 533). On the other hand, the possibility must always be considered that any products found might be of a secondary kind.

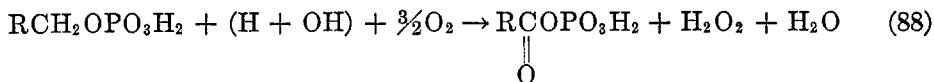
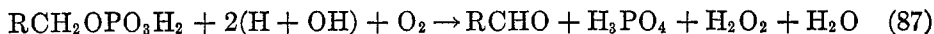
It might have been expected that there would be some specificity of attack on nucleic acids, as on many simpler compounds, and that only certain products would appear. All the available chemical evidence indicates that this is not so. X-rays, Fenton's reagent, and photoactivated hydrogen peroxide all give the same result, a general degradative attack. Among the effects are deamination, liberation of inorganic phosphate, liberation of free purine bases, decrease in optical density at 260 m $\mu$ , increase in Van Slyke amino nitrogen, decrease in purine nitrogen, and an increase in titratable acid groups (43, 96, 527, 528, 530, 531, 533). These results show that it is possible to explain the action of radiation in decreasing the structural viscosity as being due to loss of hydrogen bonding between the molecules consequent on the loss of amino groups, etc., as well as to the degradation already shown to take place (page 550). Nucleotides, nucleosides, and the purine and pyrimidine bases were also irradiated and showed the same general features as the nucleic acids. The effects of the condi-

tions of irradiation (state of aeration, pH, etc.) have been studied by the same workers, but in general without giving useful information.

### 7. Labile phosphate esters

One of the more significant results of the chemical studies is that about fifteen times more inorganic phosphate can be obtained by acid hydrolysis of irradiated nucleic acid than is formed directly by radiation. The explanation of this result is not yet known, but it has led to a possible explanation of the viscosity after-effect. Irradiation might convert the nucleic acid into a labile phosphate ester, which would be slowly hydrolyzed afterwards (532, 533, 534). Little extra phosphate is liberated spontaneously after the irradiation of nucleic acids (98, 185), but this is expected, as the phosphate in nucleic acids is diesterified except at the end groups, and the mild hydrolysis of labile phosphate esters, which would lead to a decrease in viscosity, would not yield inorganic phosphate. This theory is not unlike an earlier theory that an unstable peroxidic derivative of the nucleic acid is formed by irradiation and decomposes slowly (95), but neither theory has as yet been conclusively proved or disproved.

Whatever the relevance to the radiation chemistry of nucleic acids, the formation of labile phosphate esters is interesting in itself and has been studied with simpler compounds than nucleic acids. Both  $\alpha$ - and  $\beta$ -glycerophosphates and 3-phosphoglyceric acid have been irradiated. Inorganic phosphate appears and still more is liberated by acid treatment, although the esters produced are less readily hydrolyzed than are the products of irradiated nucleic acids (532, 534). Ethyl phosphate gives acetyl phosphate, when irradiated with x-rays in aqueous solution containing oxygen, and this decomposes slowly to give inorganic phosphate (535). In an extensive study of methyl, ethyl, *n*-propyl, *n*-butyl, and *n*-amyl phosphates it has been shown that two principal reactions take place when these are irradiated in oxygen-containing aqueous solution (626).



The second reaction becomes less favored with increasing chain length, and attack appears to occur along the hydrocarbon chain instead, possibly to give in the first place an organic peroxide. In the absence of dissolved oxygen neither the second reaction nor the formation of a peroxide takes place for any of the alkyl phosphates, but inorganic phosphate is still liberated.

## VII. FUTURE POSSIBILITIES

The radiation chemistry of organic substances may be expected to develop with equal emphasis on the chemical and the physical sides.

From the purely chemical point of view, there exists at present only scattered information, the accumulation of which is probably a prerequisite to the build-

ing up of a logical system of radiation organic chemistry. Thus there are several groups of chemicals which have never been irradiated in the pure state, and indeed few attempts have so far been made to detect all the major products of any reaction studied. Likewise there is much to be learned concerning the effects of irradiating mixtures. Relatively few non-aqueous solutions have so far been examined, and such investigations may well reveal new features of interest. For example, in considering the application of radiation chemistry as a potential synthetic method, possibly on the industrial scale, a problem is presented by the occurrence of further reactions of the first-formed radiation products. Studies on mixtures may indicate methods of controlling such reactions or of using them to good purpose.

From the physicochemical angle, one would like to know details of the primary act and to be able to trace the reactions of the ions and excited species, through the intermediate free radicals and unstable products, to the final stable products, for any and every radiation employed. At present, though use can be made of existing concepts and analogies gleaned from other branches of physical chemistry, nevertheless some results are inexplicable on current ideas. New, specifically radiation-chemical, concepts will almost certainly emerge, but again the data from which to formulate them is lacking. It is perhaps unfortunate in some ways that in the last decade (so far the most active period of radiation-chemical research) attention has been focussed so predominantly on water, which may be very untypical in its radiation-chemical behavior. However, there is now every indication that the field of radiation chemistry will broaden rapidly during the next few years. It is hoped that this review will assist such a development.

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