CHEMICAL EFFECTS OF NUCLEAR ACTIVATION IN GASES AND LIQUIDS

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I. Introduction

The first experiment on the chemical effects of nuclear activation was done by Szilard and Chalmers (*295*), who studied the behavior of radioactive iodine atoms formed in neutron irradiated liquid ethyl iodide. The observation that some of the radioactive iodine could be extracted into water was interpreted by assuming that part of the binding energy of the neutron in the iodine nucleus appeared as recoil from gamma quantum emission, leading to rupture of the bonds between the iodine atom and the rest of the molecule (*4*).

Subsequent studies of the chemical behavior of atoms activated by nuclear processes have provided information as to the secondary reactions of atoms which have freed themselves from their parent molecules, as well as to the primary processes of bond rupture.

As the subject developed several types of nuclear transformation in addition to the (n,γ) reaction were used to induce nuclear activation. In earlier work the subject was viewed primarily as an investigation of the chemical consequences of nuclear events. More recently it has been realized that nuclear activation is a useful and often unique tool for examining certain kinds of reaction mechanism. In the nuclear process a daughter atom is simultaneously energized and made radioactive. The property of radioactivity allows the energized atom to be directly identified in the reaction products. Nuclear activation permits study of the chemical behavior of atoms in energetic situations which are rather unusual from the chemical point of view. For example, recoil from nuclear emission of gamma radiation in the case of the (n,γ) reaction can give radioactive atoms with kinetic energies of the order of several hundreds of electron volts. On the whole, chemistry has been severely limited in the field of high-energy interactions. Thermal activation only permits limited data to be acquired on high-energy reactions. Collision efficiencies will start from zero as the activation energy for a given reaction is passed, rise with increasing energy of the reactants, and then fall from a maximum value as atomic velocities become too great for stable products to be formed. In thermal reactions the first part of this curve is observed, and collision efficiencies are strongly dependent on activation energies, so that as a result only reactions with minimum activation energies are attained. Nuclear activation offers a possibility of examining reaction modes over a wider range of reactant energies (*129*).

In some instances an atom undergoing nuclear activation can be located at a known point in a molecule. It is then possible to study the chemical effects of supplying localized momentum impulses, ionization, or electronic excitation within the molecule. In addition, atoms with positive charges of several units can be produced by nuclear activation, and the reactions of such charged atoms with various molecular species or the consequences of charge neutralization can be studied.

The ways in which energy of nuclear origin passes into forms of chemical interest are not clearly understood for all the nuclear processes which have been employed. In some cases lack of detailed knowledge of the physical processes has limited interpretation of the observed chemical phenomena. Furthermore, a particular nuclear process may lead to energy appearing in more than one chemically significant form. It should be pointed out, however, that many studies of the kinetics of reactions initiated by means other than nuclear activation suffer from a similar lack of exact data as to the energy and physical state of the atom at the time of reaction.

Extensive research has been done in the field in recent years. A number of reviews of the subject have appeared (*10, 14, 23, 31, 57, 60, 62, 63, 73, 94, 101, 107, 114, 172, 187, 188, 214, 217, 223, 227, 235, 257, 268, 291–293, 319, 320, 322, 324, 328*) and several symposia have been held.

A. ORIGIN OF CHEMICALLY SIGNIFICANT ENERGY FROM NUCLEAR PROCESSES

As a result of a nuclear reaction or of radioactive decay from a higher to a lower nuclear level, the atom in which the nuclear transformation has occurred may acquire kinetic energy, may become ionized, or may come to possess considerable energy of excitation of the electron shells.

1. Kinetic Energy

Kinetic energy may be imparted to an atom as a consequence of conservation of momentum during emission of quanta or particles by the nucleus.

For the case of quantum emission, formulas have been developed which give the total recoil energy as a function of the nuclear mass and the total amount of energy radiated (*10, 23, 172*). The most commonly employed reaction resulting in gamma quantum emission has been the (n,γ) reaction with thermal neutrons, in which the binding energy of the neutron is shared between the emitted quanta and the recoiling nucleus. Binding energies lie in the range ~5–10 Mev (*5*) and recoil energies have values of ~200–1500 ev.

In the case of the (n,γ) reaction several quanta are usually emitted in succession, and these gamma cascades have been extensively investigated (*11, 12, 70, 108–112, 133, 147, 148, 159, 206, 211, 212, 288*). Multiple gamma quantum emission is important for studies of the chemical behavior of atoms activated by the $n,\gamma)$ reaction because of the possibility of mutual cancellation of the individual recoils giving significantly reduced net recoil momentum in a fraction of the nuclear transformations. In part of the events in which the activated atom is found to be retained in its parent molecule after the nuclear transformation, the excited atom may have failed to rupture its bonds due to extensive momentum cancellation in the gamma cascade.

In order to examine this possibility procedures have been developed for estimating the probability that after a gamma cascade the recoiling atom would possess a net recoil momentum less than that calculated to be necessary for bond rupture. In the first papers on the subject by Cobble and Boyd (*59*) and McCallum and Maddock (*176*), the arbitrary assumption was made that the total energy available for radiation, taken as the binding energy of the neutron, was divided between 2, 3, 4, or 6 quanta of equal energy. If the additional assumptions are made that the recoil momenta can be vectorially combined and that quantum emission is isotropic, the problem can be treated as a random walk in momentum space. A distribution is found for the probability that after a given number of steps of equal length, randomly orientated with respect to each other, the final point will lie within a given radius of the starting point, the radial distance being taken as the net momentum necessary for bond rupture. Appropriate integration of these equations then yields the probability of bond rupture.

The random walk problem has been treated by Rayleigh (*238*) and Chandrasekhar (*49*). The equations have been given in integrated form suitable for radiochemical calculation (*31*), and an expression has been derived by Schweinler (*265*) for the average energy of recoil after emission of n quanta of equal energy. Since the quanta emitted in the cascades are usually of markedly unequal energies, a useful extension to the theory has been the development by O'Connor (*224*), Zvara (*343*), and Gordus *et al.* (*138*) of general solutions to a random walk with steps of unequal lengths.

A fairly well studied gamma spectrum is that of the reaction $Cl^{35}(n,\gamma)Cl^{36}$, and attempts have been made to calculate a continuous probability distribution for the kinetic energy of atoms recoiling from this reaction (*101, 138, 343*). The procedure has been to reduce the range of gamma cascades included in the calculations by omitting cascades of low probability, or by including only lines which can be consolidated into a complete cascade corresponding to the neutron binding energy. Probability distributions for the individual cascades are evaluated from the random walk procedure, and the curve of distribution of recoil energies is then constructed by adding the probabilities for individual cascades according to the frequency of their occurrence.

If the time interval between emission of the nth and the $(n + 1)$th quanta in a cascade is sufficient for the recoiling atom to have moved a distance comparable to that separating it from the rest of the molecule, then bond rupture may occur. In this case the net recoil momentum from the first n quanta alone is effective. Some knowledge of the duration of excited nuclear states is thus necessary for application of the stochastic treatment.

Considerable difficulty has been experienced in evaluating the half-lives of the excited states involved in (n,γ) cascades (*9*). Most half-lives lie in the range 10^{-13}–10^{-17} sec. The duration of a radiative transition is related to the nuclear radius, the multipolarity order of the emitted radiation, and the energy of the emitted quantum (*87, 208, 307*). Formulas have been given for calculating multipolarities (*208*), involving the change in total nuclear angular momentum I_n and the change in nuclear parity, Π, accompanying the radiative transition. The ground angular momentum of the target nucleus in the (n,γ) reaction will be known, and neutron capture will change this by $\Delta I_n = \pm\frac{1}{2}$. Angular momenta and parity values for the state corresponding to excitation of the nucleus by the full binding energy, and for various nuclear levels corresponding to observed transitions, have been determined for a number of cases and listed (*112*). Calculations based on these data show that the majority of hard transitions involve dipole radiation with half lives in the range 10^{-14}–10^{-16} sec and for this range vector addition of recoil momenta will remain valid (*59, 343*).

Such hard transitions will impart the greater part of the recoil energy to the atom. On the other hand, magnetic dipole transitions of quantum energy less than about 1 Mev have lifetimes greater than 10^{-14} sec and quanta of this energy will often be present in the cascade (*112*).

In general gamma cascades from (n,γ) reactions are so far known in only a few cases in sufficient detail to justify full calculations of recoil energy spectra. But as studies proceed it can be expected that energy spectra will be evaluated for a number of isotopes commonly encountered in chemical studies.

Kinetic energy may also be imparted to an atom when a positive charge, acquired as a result of a nuclear process, is neutralized by transfer of electrons from neighboring atoms. Magee and Gurnee (*195*) have treated the case of HBr^{+z}, in which the positive charge has been acquired from an Auger cascade initiated by $Br^{80m} \rightarrow Br^{80} + h\nu$, and have found that during discharge of HBr^{4+}, for example, the available maximum of 51 ev will not usually be imparted to the ion pair as kinetic energy after the first neutralization act. About 10–20 ev will usually appear as kinetic energy and the remainder as energy of electronic excitation.

In the case of (n,γ) reactions with thermal neutrons the source of kinetic energy is the binding energy of the neutron. When the nucleus is struck by a fast neutron or charged particle, part of the energy of the incident particle will be transferred as kinetic energy to the struck nucleus. In this case it is possible to achieve kinetic energies of recoil in the range 10^3–10^6 ev. Formulas have been developed for calculating recoil energies for reactions with monoenergetic fast particles (*73*, *172*, *265*), and Schweinler (*265*) has discussed the case of irradiation in the spectrum of fast neutrons found in a nuclear reactor.

Formulas have also been developed for calculation of the recoil energy from alpha or proton emission in radioactive decay (*10*, *23*, *172*). In this case energies of tens to hundreds of kev may be attained.

The case of recoil from beta emission has been treated by Libby (*172*), assuming no angular correlation between beta particle and neutrino. Edwards and Davies (*73*) have discussed the case in which such a correlation exists. In the absence of correlation the recoil energy spectrum has a broadly rounded peak and extends up to a maximum value of $548(E_{\beta\,\max}/M_e) + 536[(E_{\beta\,\max})^2/M_e]$ ev, where M_e is the mass of the emitting atom, and the maximum beta particle energy, $E_{\beta\,\max}$, is in Mev. For a 0.5 Mev beta emitter of mass 50 the maximum recoil energy will thus be about 8.2 ev. If the beta particle and neutrino tend to be emitted in the same hemisphere the recoil energy spectrum will tend to be fairly sharply peaked towards the higher energies. If emission in opposite hemispheres is preferred the spectrum declines slowly from a maximum at zero recoil energy.

Extensive work has been done to establish the nature of the correlation between beta and neutrino emission (*14*, *121*, *140*, *141*, *152*, *270*, *277*) and Konopinski has reviewed the subject (*154a*).

Baulch and Duncan (*14*) have calculated the energy spectrum of recoils from beta emission by C^{14} for different assumed beta-neutrino interactions.

Recoil from nuclear fission gives fragments with recoil energies totaling $\sim$170 Mev in the case of U^{235}.

2. Ionization

An important process leading to loss of electrons is internal conversion of gamma quanta in isomeric transitions or (n,γ) reactions. An Auger or vacancy cascade following upon loss of a K or L shell electron can result in a charge of several units at the periphery of the atom (*28*, *64*, *71*, *231*, *275*, *337*). Electron capture by the nucleus leading to a vacancy in an inner shell can also initiate an Auger process.

Measurements of the charge acquired by halogen atoms as a result of (n,γ) reactions and isomeric transition have been made by Wexler and Davies and their collaborators (*308*, *312*, *314*, *315*, *340*). In later work charge spectrometry has been developed in order to investigate the relative probabilities of loss of one, two, three, or more electrons following the nuclear event. This technique, which has been described by Snell, Pleasonton, and Carlson (*275*, *280*), involves a source volume containing the gas in which the nuclear event is to occur, a magnetic analyzer, and an electron-multiplier detector. The gas must be at a sufficiently low pressure to give a very small probability of charge transfer during collision.

In the case of nuclear processes that give rise to loss of an inner shell electron it is found by charge spectrometry that the Auger cascade leads to a charge spectrogram with relatively low probabilities at charge +1, rising to a maximum at about 8 charge units, and then falling again towards higher charge numbers. To avoid complications of charge sharing between fragments of a molecule decomposed by the charging process, charge acquisition from nuclear processes is best studied in monatomic gases. The isomeric transition $Xe^{131m} \rightarrow Xe^{131}$ has been studied by Snell *et al.* (*233*, *280*). In this case the Auger cascade gives a most probable charge value of +8 units, this charge being acquired in about 20% of events.

When a change in charge, ΔZ, occurs on the nucleus of an atom undergoing radioactive decay, there is a change in the nuclear field strength causing expansion of the extranuclear shells when $\Delta Z < 0$ and contraction when $\Delta Z > 0$. If the rearrangement of the electron shells is slow by comparison with the nuclear process then considerable electronic excitation can occur (*13*, *46*, *86*, *106*, *153*, *199*, *264*, *267*, *327*, *336*, *337*) and ionization may result. Ionization from this cause has been termed "shake-off" (*275*).

Charge spectrograms have been obtained by Snell, Pleasonton, and Carlson for β^- emission (*45, 46, 232, 275, 276, 278, 280, 282*) and have been found to differ markedly in shape from those obtained when the charging process is initiated by loss of an inner electron. For β^- (or β^+) emission there is usually no electron loss so that charge $+1$ (or -1) dominates in the charge spectrum, followed by a distribution resulting from loss of outer electrons, dropping off sharply towards higher charge values. For example, in the decay $Kr^{85} \rightarrow Rb^{85} + \beta^-$ a charge of $+1$ is found in 79% of cases, $+2$ in 11%, and at $+6$ the probability has dropped to 0.7% (*46*). In the case of the transitions studied by Carlson *et al.* (*46*) there is a good agreement with the predicted extents of ionization given on theoretical grounds by Winther (*327*) and Green (*106*). Charge spectrometry has also been used to study the charging process consequent upon electron capture (*279*) and in mixed decay schemes (*282*).

From the comparison of charge spectra given above it seems that isomeric transition with an Auger cascade should have violent chemical consequences for any molecule in which it occurs, whereas the effects of "shake-off" should be much milder.

Emission of charged particles from the nucleus may cause ionization of the electron shells by processes other than shake-off. There is a finite probability that the emitted particle may interact directly with one of the extranuclear electrons. The direct ejection of an electron by a beta particle passing through the shells has been studied theoretically by a number of workers. Migdal (*199*), Feinberg (*86*) and Winther (*327*) conclude that the probability of direct ejection of an electron by a beta particle is two or three orders of magnitude less than the probability of ionization by shake-off. Grard (*105*), however, suggests that the coulombic interaction between beta particle and extranuclear electron may be more important for heavy elements.

Ejection of an electron in alpha particle emission is more probable than in beta emission. The charge on atoms of Ra D recoiling after alpha emission by Ra C has been measured and found to be $+2$ (*181*), and a similar charge is found in the decay $Rn \rightarrow Ra\ A + \alpha$ (*213*).

Wolfsberg and Perlman (*337*) have suggested that the Auger cascade should not necessarily be treated as a process involving two electrons, one of which undergoes a transition to a vacant orbital of lower energy while the other is raised to the continuum. Some of the outer electrons have velocities small compared with those of Auger electrons ejected from inner shells, so that the effective nuclear charge is suddenly changed and the outer electrons may experience a shake-off similar to that induced by emission of a charged particle from the nucleus. This polyelectronic treatment predicts a larger charge from the Auger effect than that expected on a 2-electron basis. Snell and Pleasonton have obtained charge spectrograms of Cl^{37} resulting from electron capture in A^{37} (*275, 277*) and find a 10% probability for Cl^{5+}, 1.8% for Cl^{6+}, and 0.4% for Cl^{7+}. The usual 2-electron Auger mechanisms predict a maximum charge of +5, so that Snell and Pleasonton's figures may perhaps be interpreted as supporting the polyelectronic process. However, increase of multiplicative steps by Coster-Kronig transitions between subshells must also be taken into account (*280*).

In the case of atoms recoiling with energies in the multi-kev range auto-ionization may occur. It was pointed out by Bohr (*20, 21*), Knipp and Teller (*149*) and Lamb (*158*) that electrons whose peripheral velocity was less than that of the recoiling nucleus should be shed. This results in $\sim 10^3 \times m$ ev as the upper limit of the energy range in which such ionization will not occur (*172*), where m is the mass of the recoil in a.m.u. Ionization by this means will therefore only be of importance in cases of highly energetic recoils from heavy particle emission, fission, or nuclear reactions with fast incident particles. In the case of the most probable mode of fission of U^{235} the lighter fragment has a recoil velocity of $\sim 1.5 \times 10^9$ cm/sec and this will cause ~10–20 electrons to be stripped off by auto-ionization (*73*).

Starodubtsev and Romanov (*283*) have given a general review of the mechanisms whereby ionization of electron shells may be produced by nuclear transformation.

3. Electronic Excitation

As mentioned in Section I,A,*2* electronic excitation can be expected to occur in those processes in which a change of nuclear charge takes place more rapidly than the readjustment of the electron shells. In some cases the electron cloud will contract adiabatically to the configuration corresponding to the new charge, but sometimes excited states will result in which the energy of excitation has been derived from the particle emission.

Serber and Snyder (*267*) conclude that for the case of nonadiabatic emission average, the energy of electronic excitation is given approximately by $E_{\text{exc}} = 24.47Z^{1/3}(Z' - Z)^2$ ev, where Z, Z' are the nuclear charges before and after the emission. For a C^{14} atom beta particle emission thus imparts an energy of 59 ev to the electron shells, and considerably more energy will be supplied in the case of the heavier elements.

The theoretical treatments of Migdal (*199*), Winther (*327*) and Green (*106*) allow calculations to be made of the distribution of energy of electronic excitation resulting from particle emission. This distribution has been calculated for the cases $H^3 \rightarrow (He^3)^+$ and $He^6 \rightarrow (Li^6)^+$, using the sudden perturbation method of Migdal and Winther. The distributions show a rapid decline of probability with increase of excitation energy, 67–70% of the daughter ions being formed in the ground state (*313*).

However, 25% of the $(He^3)^+$ ions have 20.5 ev of excitation energy, while 17% of the Li^+ possess about 60 ev. Kołos (*153*) has compared the results of calculations of the probability of formation of ground state daughter ions from the He^6 beta decay using self-consistent field wave functions with those obtained by previous authors using one-electron hydrogen-like orbitals.

Baulch *et al.* (*15*) have discussed methods of assessing the electronegativities of atoms in excited states after nuclear decay. Pauling-Mulliken methods are used to calculate the electronegativities. Heats of formation of excited molecules and the fractional charges on constituent atoms are thus estimated. The method has been applied to the formation of $Bi(CH_3)_4^+$ from $Pb(CH_3)_4$ by beta decay, and it has been found that an enhanced charge should be present on the Bi atom in the 4-methyl compound by comparison with $Bi(CH_3)_3$, which may account for the ease of hydrolysis of the gaseous products of beta decay of lead tetramethyl.

Electronic excitation may also occur during neutralization of the charge acquired as a result of nuclear transformation. Magee and Gurnee (*195*) have pointed out that such excitation may occur, due to crossover of the potential energy curves for an ion-molecule pair with curves for excited states of one member of the ion-pair which results from charge transfer. As mentioned in Section I,A,*2*, during the reaction $HBr^{+4} + HBr \rightarrow HBr^{+3} + HBr^{+1}$ as much as 30–40 ev may be available for excitation of the electrons of the products.

4. Summary

To sum up the present section it can be seen that nuclear activation can supply kinetic energy, charge, and energy of electronic excitation to marked atoms within limits which are wide from the chemical point of view. Kinetic energies can vary in the range of a few ev for beta emission to many hundreds of kev for reactions with fast incident particles. Electron loss can be a relatively mild process involving perhaps only a 10% probability of producing a charge of +2 units in the case of shake-off, or it can be a violent process readily causing loss of 8–20 electrons in the case of internal conversion or nuclear fission. Electronic excitation from nonadiabatic particle emission may considerably exceed the first and second ionization potentials of the atom.

One of the greatest drawbacks to the use of nuclear activation in chemical studies is the occurrence of more than one mode of energization in a single nuclear process. Thus, for example, a marked atom from an (n,γ) reaction will have recoil energy, but there is also a considerable probability of charge acquisition by internal conversion of some of the softer quanta in the gamma cascade (*134*, *210*). Neutralization of the charge of this atom during its recoil may in turn cause excitation of its extranuclear electrons. As a second example, an atom may emit soft gamma rays during an isomeric transition. The energy of recoil from the quantum emission may be too small to be chemically significant. Nevertheless conversion of the quanta may lead via a vacancy cascade to a charge of several units on the periphery of the atom, and neutralization of this charge may then inpart a kinetic energy four or five times greater than the energy of chemical bonds in the vicinity.

The studies reviewed in subsequent parts of this article show that despite the complicated nature of nuclear activation the chemical consequences of this process can often be successfully related to the energetics of the nuclear event.

B. Loss of Energy of Atoms Activated in Nuclear Processes

Kinetic energy is lost from a recoiling ion by elastic or inelastic collisions with atoms or molecules of the environment (*18*, *72*), or by interaction of the ion with electrons of the medium in which recoil occurs.

For ions whose velocity is much greater than the velocity v_e, of the outermost electrons of a struck atom, excitation and ionization by interaction with electrons of the medium account for practically all the energy loss. At recoil velocities considerably smaller than v_e elastic and inelastic collisions with the struck atom as a whole become increasingly predominant.

Seitz (*266*) has suggested that the limiting kinetic energy, $E_{\min}$, for excitation of electrons of the medium by a recoiling atom of mass m is given approximately by $(m/m_e)I_{\text{exc}}$, where m_e is the mass of an electron and I_{exc} is the lowest electronic excitation level, corresponding to the lower limit of the main optical absorption band. For insulators $I_{\text{exc}} \approx$ 4–5 ev, so that for an atom of mass 50, for example, $E_{\min} \approx 46$ kev. Loss of energy by interaction with electrons of the medium will thus only be important for ions recoiling from reactions with fast particles, from alpha, proton, or neutron emission, or from nuclear fission. In calculations of the amounts of energy delivered up to the medium by excitation or ionization, the approximation is often made that for $E_{\text{recoil}} > E_{\min}$ the recoil loses energy only by electronic events, and for $E_{\text{recoil}} < E_{\min}$ all energy is lost by elastic collisions (*18*).

The theory of energy loss from a recoiling atom or ion by elastic collisions has been well established (*87*, *97*, *172*, *230*, *306*).

In the intermediate range, for which $v_{\text{recoil}} \approx v_e$, the recoiling atom will go through many cycles of electron capture and loss as it slows down. The considerable amount of work which has been done on the exchange process for gaseous ions of hydrogen and helium has been reviewed by Allison (*3*). The total number of collisions in which the neutral atom is formed is a function of the stopping power of the medium (which depends on the energy of the moving ion) and the energy-dependent cross-section for completion of the electron capture and loss cycle. As an example, an H atom in slowing down from 300 kev to 9 kev in hydrogen gas goes through $\sim$2000 charge-changing cycles. Measurements have been made of the equilibrium fractions of -1, 0, and $+1$ states in hydrogen or helium beams passing through various gases (*3*). The equilibrium fractions are a function of the recoil energy and the nature of the medium. In the energy region above $\sim$100 kev in hydrogen gas the H^+ state predominates, but at energies below $\sim$10 kev the neutral atom is present to about 90%, the H^+ state having dropped to a little below 10%. This finding has important implications for chemical studies with H^3 atoms activated by the reactions $Li^6(n,\alpha)H^3$ $[E_{recoil} = 2.730$ Mev] or $He^3(n,p)H^3$ $[E_{recoil} = 0.192$ Mev]. When the tritium atom has cooled to energies at which it can react to form stable chemical bonds it would seem from the above picture that it should exist predominantly as the neutral atom (*67, 77*). Rowland *et al.* (*247*) have pointed out, however, that there is a possible positive ion contribution when H^3 recoils through a medium containing molecules of ionization potential greater than the first ionization potential of hydrogen.

The data on equilibrium fractions do not as yet extend down to the few ev range in systems of chemical interest. Fite *et al.* (*89, 90*) have measured the cross-sections for the transfer reactions $p + H \rightarrow H + p$ and $p + H_2 \rightarrow H + H_2^+$. The cross-section for neutralization of the proton in atomic hydrogen has been measured down to 100 ev. As the energy declines from 10 kev to 100 ev the cross-section rises by a factor of approximately 5. The neutralization in molecular hydrogen has been studied from 10 kev down to 400 ev and in this range the cross-section declines by a factor of 8. Simons *et al.* (*215*) have found a large cross-section for neutralization of H^+ in the 2–150 ev range in organic gases, but not in helium or argon. This finding emphasizes the current lack of data from which we can derive the equilibrium fractions of the charge states of hydrogen atoms recoiling through gases or liquids containing various compounds. The situation is no better for recoiling species other than hydrogen.

Some light is thrown on the way in which the cross-sections for positive charge neutralization vary with ion velocity by the resonance rule (*197, 209*), which states that maximum cross-section occurs when $\Delta E/h \approx v/a$, where ΔE is the net energy defect, v is the relative velocity of the interacting particles, and a is the range over which interaction occurs. Wolfgang *et al.* (*77*) have used this rule and the energies of charge transfer processes in methane to suggest that in the terminal part of a recoil track neutralization probability for $(H^3)^+$ will become maximal, whereas ionization probability for H^3 will decline.

Energy of electronic excitation from nuclear transformation may be lost from an atom before it can affect its chemical behavior. Baulch and Duncan (*13, 15*) have discussed the conditions favoring isothermal decay, in which energy of electronic excitation is lost before the bond between the atom and the remainder of the molecule is affected, and adiabatic decay in which the chemical behavior of the daughter is not that of the atom in its ground state. Evidence quoted by these authors from pre-dissociation spectra of I_2, S_2, AlH, CaH, InH, and TlH at high argon pressures or in a magnetic field (*95, 113, 154, 299, 300, 304*) indicates that in these cases dissociation is induced by collision and that metastable states can have lives as long as 10^{-6} sec. These experiments support the conclusion that the lifetime depends on the stability of the excited state itself and on whether chemical reaction is induced before de-excitation can occur.

II. Primary Processes Leading to Bond Rupture

A. GENERAL CONSIDERATIONS

The earliest experiments on the chemical effects of nuclear activation were concerned with the way in which the activated atom ruptured its bonds with the molecule in which it was located before the nuclear event, and this problem has remained an important aspect of the subject. It would be very desirable to know accurately the fraction of events in which the atom failed to rupture its bonds as a result of possessing too small an energy of activation, or too small a degree of ionization. If this fraction were then subtracted from the fraction of labeled daughter atoms found in the parent molecule at the end of the experiment, we would know the number of events in which the activated atom had freed itself from its initial bonds and, after a period of freedom, had recombined to form the parent type molecule. Such information is required to evaluate the relative probability of recombination processes.

In order to measure the probability of primary bond rupture we need to arrange experimental conditions so that the chances of recombination to reform the parent type molecule are minimal. In the case of nuclear processes giving very small recoil energies (e.g., internal conversion of soft gamma quanta, as in $\mathrm{Br}^{80m} \rightarrow \mathrm{Br}^{80} + h\nu$) the cage of solvent molecules around the nuclear transformation site in a liquid may favor recombination, and experiments should then be done in the gas phase. Where kinetic energies are sufficiently large to separate primary fragments in a liquid system, the probability of recombination of the fragments can be reduced by working with very low concentrations of the parent molecule in an "inert" diluent. By an inert diluent is meant a substance with which the activated atom will not combine to form a species impossible to separate from the parent molecule before radioactivity measurements. Sometimes it may be useful in gas or liquid systems to add a trapping substance with which the radioactive atom will combine in a highly probable reaction after primary bond rupture, giving a readily separable compound. Radical scavengers may be introduced to lower the probability of recombination of the activated atom with one of the radicals produced during its recoil. In gas phase studies it is often useful to add inert moderators which will remove kinetic energy from the recoil during collisions, without forming radioactive species which could not be separated from the target substance.

As a result of the various types of nuclear activation described earlier, the following mechanisms may lead to primary bond rupture:

(a) The activated atom may acquire sufficient kinetic energy to rupture its bonds [e.g., in (n,γ) reactions, or in fast particle reactions or in α, β, p, or n emission].

(b) Sufficient electrons may be lost from the outer shells to cause bond rupture (e.g., in vacancy cascades or shake-off processes). The possibility must be borne in mind that the charge may spread over the molecule before the activated atom can break its bonds, and a number of different modes of molecular disintegration may occur.

(c) Acquisition of electronic excitation from nuclear transformation may induce molecular dissociation (e.g., in nonadiabatic beta particle emission). Once again, spreading of the excitation over the molecule may give rise to several decomposition products.

B. Bond Activation by Recoil

In the case where an atom in a polyatomic molecule receives a momentum impulse from a nuclear transformation, we have to consider the way in which energy is transferred to the bond or bonds attaching the activated atom to the molecular residue, and to the molecular residue itself.

Gordus and Hsiung (*102a*) have treated this problem on the basis of classical mechanics, using the following assumptions:

(a) The molecule is regarded as a group of point masses, the atoms linked together with springs and thus capable of undergoing independent constrained motions in addition to the translational and rotational motions of the molecule.

(b) The recoil energy is large compared with the thermal energy of the molecule.

(c) The momentum impulse, Q, is received by the atom undergoing nuclear transformation in a time period so short that other atoms in the molecule do not increase their translational velocity. This assumption requires that the duration of the momentum impulse should be less than the time required for dissociation, i.e., less than the period of a single vibration, $\sim 10^{-14}$ sec.

(d) The momentum impulse, Q, supplied by the recoiling atom can be resolved into a component, Q_{R}, perpendicular to the line joining that atom to the center of the molecule, and Q_{V}, in a random direction. Q_{R} causes rotation of the molecule, while Q_{V} results in a molecular vibration dependent on bond strengths and moments of inertia. In addition to the effect of recoil on vibrational states there is a rotational effect on potential energy due to stressing of the bonds by centrifugal forces. This contribution is evaluated by treating the atoms as simple harmonic oscillators about their equilibrium positions. The centrifugal force vector is resolved into a component in the direction of a given bond, causing bond stretching, and a component at right angles to the bond causing a bending vibration.

(e) When the energy laid down in a given bond, as evaluated on the basis of the above assumptions, exceeds the bond energy, E_{b}, then bond rupture is considered to result.

The total internal energy increase is given by:

$$E_{\text{int}} = \tfrac{1}{2}\Sigma m_i(\boldsymbol{\omega} \times \mathbf{r}_i) \cdot (\boldsymbol{\omega} \times \mathbf{r}_i) + \tfrac{1}{2}\Sigma m_i v_i^2 + V(\mathbf{r}_i) - V(\mathbf{a}_i) \qquad (1)$$

where $\boldsymbol{\omega}$ is the angular motion of the molecule about its center of gravity, $\mathbf{r}_i$ is the position vector for the i type atom with the center of gravity as origin, v_i is the vibrational velocity of the ith atom with respect to the molecule, $\mathbf{a}_i$ is the vector defining the equilibrium position of the ith type atom, and V represents potential energy as a function of spatial position. The first term on the right hand side of Eq. (1) is the rotational energy, the second term is the vibrational energy, and the last is the potential energy of the molecule.

By evaluating the terms of Eq. (1) expressions have been derived for $E_T{}^\circ$, the net recoil energy which must be received by the atom undergoing nuclear transformation in order that bond rupture should occur *(102a)*. Table I shows values of $E_T{}^\circ$ necessary for C—Br rupture in organic bromides as calculated on the basis of these expressions. The original paper lists similar values for C—I and C—Cl bond rupture in chlorides and iodides.

On the basis of the calculated values of $E_T{}^\circ$ and the spectra of recoil energies from given (n,γ) reactions, calculated by the stochastic methods of Section I,A,*1*, it should be possible to make an estimate of the percentage of nuclear events leading to bond rupture. Some comparisons of observed and calculated frequencies of bond rupture are given in Section II,C.

The Gordus-Hsiung treatment assumes that the duration of the momentum impulse is short by comparison with the vibration period, $\sim 10^{-14}$ sec. As mentioned in Section I,A,*1*, hard transitions in (n,γ) cascades

TABLE I
MINIMUM NET RECOIL ENERGIES, $E_T°$, REQUIRED FOR C—Br BOND RUPTURE IN ORGANIC BROMIDES (*102a*)

Molecule	Molecular weight	$E_T°$ (ev)
CH_3Br	95	20.74
CD_3Br	98	18.54
C_2H_5Br	109	15.14
CF_3Br	149	7.38
CH_2Br_2	174	6.14
CCl_3Br	200	4.06
$CHClBr_2$	209	4.93
CF_2Br_2	210	4.90
CCl_2Br_2	244	3.64
$CHBr_3$	253	4.76
CBr_4	332	2.98

have half-lives in the range 10^{-14}–10^{-16} sec., and these steps impart the bulk of the recoil energy, so that in many instances of the (n,γ) reaction the Gordus-Hsiung treatment will be valid. For beta emission, the time taken for a relativistic electron to leave a shell of electrons bound by a charge Ze is:

$$t \approx \frac{\hbar^2}{Zm_e e^2 c} \tag{2}$$

i.e., $t \lesssim 10^{-16}$ sec., so that the assumption of short duration of the momentum impulse is valid. Nevertheless, some intramolecular momentum transfer will occur, and for this reason calculated values of $E_T°$ may be low. The error in $E_T°$ may be expected to increase with molecular complexity.

From Table I it can be seen that $E_T°$ declines as the molecular weight increases. Qualitatively this can be visualized as a tendency for a light recoil readily to sever its bonds with a heavy residue, whereas a heavy recoil will tend to carry a light residue with it. This effect was predicted in work by Suess (*289*), who had calculated that for a diatomic molecule the energy of activation of the bond is related to the energy of recoil, E_r, by:

$$E_i = E_r \frac{(M - m)}{M} \tag{3}$$

where m is the mass of the recoil and M is the mass of the molecule.

Steinwedel and Jensen (*284*) have also calculated the fractional distribution of internal energy between the vibrational states and rotational states, and applied a quantum mechanical approach to the problem. More recently Svoboda (*290*) has discussed the effect of inelastic internal collisions by the recoiling atom on the probability of bond rupture. Wolfsberg (*336*) has used a quantum-mechanical treatment to evaluate the average vibrational and rotational energies supplied to a molecule as a result of nuclear recoil, and to calculate the probability of exciting to a given vibrational state from the lowest state. The same author has used this treatment to calculate the probability of dissociation of $CH_3—C^{14}H_3$ by recoil from the reaction $C^{14} \rightarrow {}_{-1}\beta + N^{14}$. Assuming that the parent molecule is in the ground rotational vibrational state and that the dimensions and force constants of both parent and daughter molecules are the same, the method predicts that the C—N bond energy of 2.1 ev will be exceeded whenever $E_R > 3.57$ ev. The method of Gordus *et al.*, outlined above, gives a value of $E_R > 3.53$ ev, when the assumptions are made that the CH_3 and NH_3 groups are rigid (*102b*).

C. Bond Rupture in the (n,γ) Reaction

The earliest experiments on bond rupture consequent on the (n,γ) reaction were done with organic halides in the gas phase where no cage of adjacent molecules restrains the activated atom. Results from various authors are shown in Table II.

Efficiencies of bond rupture are very high, usually being over 90%. This result might be expected with radiohalogen atoms recoiling with kinetic energies of hundreds of ev, and having in some cases a positive charge from conversion of the gamma quanta (*314*). The results show, however, that the true efficiencies for bond rupture are obtained only by working at micron pressures, where the probability of a retention-causing collision in the gas is low before the recoils strike the wall of the vessel and are trapped (*314*), or by adding the efficient radical scavenger NO at sufficient pressures to allow it to act as a moderator (*102*). Under these conditions the bond rupturing process is found to be more than 99% efficient. At higher pressures addition of elementary halogen as a trapping agent for the recoils in the case of C_2H_5I reveals a similar efficiency for the rupturing mechanism (*136*), although the results shown for the bromine compounds irradiated at mm Hg pressures in presence of elementary bromine or HBr (*35*, *81*) indicate that secondary reaction has occurred.

The high bond rupturing efficiency of the $Br^{79}(n,\gamma)Br^{80m}$ and the $I^{127}(n,\gamma)I^{128}$ reactions indicates either that mutual cancellation of the recoil momenta in the course of the gamma cascade cannot be an important factor in these processes, or that ionization due to internal conversion occurs in about 99% of events. Wexler and Davies (*314*) found that the percentage of radiohalogen atoms carrying positive charges after ejection from gaseous ethyl bromide or iodide at micron pressures was 12% for $Br^{79}(n,\gamma)Br^{80m}$, 25% for $Br^{81}(n,\gamma)Br^{82}$ and 50% for $I^{127}(n,\gamma)I^{128}$. Clearly

TABLE II

PERCENTAGES OF RADIOHALOGEN ATOMS RETAINED IN ORGANIC COMBINATION AFTER NEUTRON IRRADIATION OF ORGANIC HALIDES IN GAS PHASE

Target irradiated[a]	Nuclear reaction	% Radiohalide in organic combination	Reference
$C_2H_5Br(390) + Air(370)$	$Br^{79}(n,\gamma)Br^{80m}$	4.5	*(171)*
$C_2H_5Br(137\text{–}217) + HBr(10.5\text{–}203)$	$Br^{79}(n,\gamma)Br^{80m}$	3–18	*(325)*
$C_2H_5Br(1 - 3 \times 10^{-3})$	$Br^{79}(n,\gamma)Br^{80m}$	<1%	*(314)*
$C_2H_5Br(10\text{–}15) + NO(700)$	$Br^{79}(n,\gamma)Br^{80m}$	0.33	*(102)*
$CH_2BrCH_2Br(40) + Air(720)$	$Br^{79}(n,\gamma)Br^{80m}$	6.9	*(171)*
$CH_3Br(760) + Br_2(10)$	$Br^{79}(n,\gamma)Br^{80m}$	3.9–4.1	*(104)*
$CH_3Br(10\text{–}15) + NO(700)$	$Br^{79}(n,\gamma)Br^{80m}$	0.25	*(102)*
$CD_3Br(10\text{–}15) + NO(700)$	$Br^{79}(n,\gamma)Br^{80m}$	0.20	*(102)*
$CH_2Br_2(10\text{–}15) + NO(700)$	$Br^{79}(n,\gamma)Br^{80m}$	0.115	*(102)*
$CHBr_3(10\text{–}15) + NO(700)$	$Br^{79}(n,\gamma)Br^{80m}$	0.048	*(102)*
$CF_3Br(10\text{–}15) + NO(700)$	$Br^{79}(n,\gamma)Br^{80m}$	0.105	*(102)*
$CF_2Br_2(10\text{–}15) + NO(700)$	$Br^{79}(n,\gamma)Br^{80m}$	0.093	*(102)*
$CHClBr_2(10\text{–}15) + NO(700)$	$Br^{79}(n,\gamma)Br^{80m}$	0.087	*(102)*
$CCl_3Br(10\text{–}15) + NO(700)$	$Br^{79}(n,\gamma)Br^{80m}$	0.066	*(102)*
$CBr_4(10\text{–}15) + NO(700)$	$Br^{79}(n,\gamma)Br^{80m}$	0.031	*(102)*
$1{,}1\text{-}C_2H_4Br_2(10\text{–}15) + NO(700)$	$Br^{79}(n,\gamma)Br^{80m}$	0.173	*(102)*
$C_6H_5Br(2) + Br_2(6 \times 10^{-2})$	$Br^{79}(n,\gamma)Br^{80}$	5.56	*(81)*
$C_6H_5Br(2) + Br_2(6 \times 10^{-2})$	$Br^{79}(n,\gamma)Br^{80m}$	5.89	*(81)*
$C_6H_5Br(2) + Br_2(6 \times 10^{-2})$	$Br^{81}(n,\gamma)Br^{82}$	5.40	*(81)*
$n\text{-}C_3H_7Br(70) + Br_2(3.5 \times 10^{-2})$	$Br^{79}(n,\gamma)Br^{80}$	5.28	*(81)*
$n\text{-}C_3H_7Br(70 + Br_2(3.5 \times 10^{-2})$	$Br^{79}(n,\gamma)Br^{80m}$	5.74	*(81)*
$n\text{-}C_3H_7Br(70) + Br_2(3.5 \times 10^{-2})$	$Br^{81}(n,\gamma)Br^{82}$	5.43	*(81)*
$C_2H_5I(80)$	$I^{127}(n,\gamma)I^{128}$	2.9–6.8	*(136)*
$C_2H_5I(80) + I_2(0.2)$	$I^{127}(n,\gamma)I^{128}$	1.1–1.4	*(136)*
$C_2H_5I(10\text{–}15) + NO(700)$	$I^{127}(n,\gamma)I^{128}$	0.82	*(102)*
$CH_3I(10\text{–}15) + NO(700)$	$I^{127}(n,\gamma)I^{128}$	1.09	*(102)*
$CD_3I(10\text{–}15) + NO(700)$	$I^{127}(n,\gamma)I^{128}$	0.68	*(102)*
$CF_3I(10\text{–}15) + NO(700)$	$I^{127}(n,\gamma)I^{128}$	0.12	*(102)*
$CH_2I_2(10\text{–}15) + NO(700)$	$I^{127}(n,\gamma)I^{128}$	0.068	*(102)*
$n\text{-}C_3H_7I(10\text{–}15) + NO(700)$	$I^{127}(n,\gamma)I^{128}$	0.66	*(102)*
$i\text{-}C_3H_7I(10\text{–}15) + NO(700)$	$I^{127}(n,\gamma)I^{128}$	0.30	*(102)*
$n\text{-}C_4H_9Cl(103)$	$Cl^{37}(n,\gamma)Cl^{38}$	9.4–12.1	*(51)*
$n\text{-}C_4H_9Cl(95\text{–}107) + HCl(95\text{–}102)$	$Cl^{37}(n,\gamma)Cl^{38}$	10.6–11.5	*(51)*

[a] Figures in parentheses are gas pressures in mm Hg.

ionization alone cannot account for the observed efficiencies of bond rupture. Furthermore very similar bond rupturing efficiencies were obtained in experiments shown in Table II in which the $Br^{79}(n,\gamma)Br^{80m}$ and $Br^{81}(n,\gamma)Br^{82}$ reactions were compared *(81)*, despite the differences in ionization.

Libby (*171*) has used ethanol as an "inert" diluent for CBr_4 irradiated with neutrons in the liquid state and has found that the percentage of Br^{80m} retained in organic combination drops from 28 ± 5% at 1.15 mole % CBr_4 to 0 ± 2% at 0.064 mole %. This finding supports the conclusion from the gas phase experiments as to the very high efficiency of bond rupture in the $Br^{79}(n,\gamma)Br^{80m}$ reaction.

As yet relatively few attempts have been made to relate measured efficiencies of bond rupture in gas or liquid systems to the spectra of net recoil energies calculated by the stochastic methods of Section I,A,*1*. Gordus *et al.* (*102*) have calculated the net gamma ray energies, $E_{\gamma 0}$, necessary for bond rupture by the methods discussed in connection with Eq. (1), and have plotted these against the observed organic yields of Br^{80} in various organic bromides after the $Br^{79}(n,\gamma)Br^{80}$ reaction. The results are shown in Fig. 1. The data seem to support the general view that retention of the Br^{80} atom in organic combination is related to the energy distribution of recoils from the (n,γ) reaction. As yet insufficient data on the $Br^{79}(n,\gamma)Br^{80}$ gamma cascade are available to allow a full recoil energy spectrum to be evaluated for this reaction, using the random walk procedure. For purposes of rough comparison, however, the dotted line in Fig. 1 corresponds to the recoil probability distribution for the $Cl^{35}(n,\gamma)Cl^{36}$ reaction.

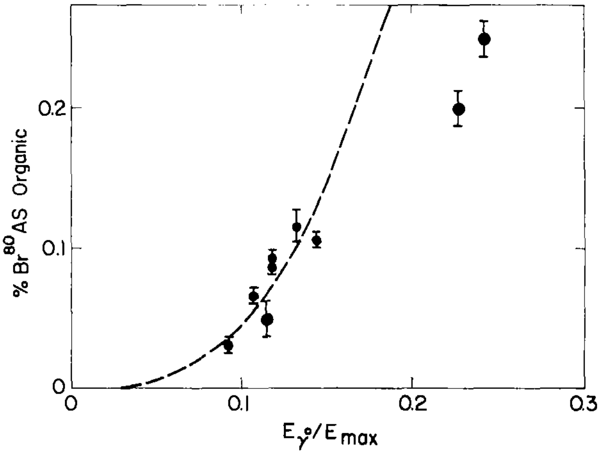


FIG. 1. Organic retention of Br^{80} as a function of net gamma recoil energy required for bond rupture (*102*). Dashed curve corresponds to calculated probability distribution for the $Cl^{35}(n,\gamma)Cl^{36}$ process.

It must be remembered that the values of $E_T{}^\circ$ used in Fig. 1 were calculated without taking into account any loss of electrons by internal conversion of the (n,γ) quanta. The value of $E_T{}^\circ$ required for bond rupture of the positively charged molecule differs from that required for the neutral molecule. For example, $E_T^\circ = 2.77$ Mev for $CH_3I^+ \rightarrow CH_3^+ + I$ and 2.55 Mev for neutral CH_3I (*102*).

Assuming 25 ev as the total energy of phosphorus-oxygen bonds in tributyl phosphate (TBP), applying Eq. (3) and selecting two probable gamma cascade schemes for the reaction $P^{31}(n,\gamma)P^{32}$, it has been shown by the stochastic procedure outlined in Section I,A,*1* that failure to rupture all bonds should occur in 2.2–3.5% of events (*36*). In such a complicated system di- and mono-P^{32}-esters are likely to be formed as well as TBP^{32} by failure to rupture bonds, as well as by "hot" and "thermal" secondary processes (see Sections III,B and III,C). Irradiation of TBP in heptane or benzene as "inert" diluents, and use of radical scavenger techniques to estimate the contribution to the organic P^{32} yield from thermal reactions has led to the value of 2–4% being obtained for the failure to rupture all bonds in TBP, in good accord with the predicted values (*272*).

Trimethyl phosphine gas has been irradiated in the presence of argon as a moderator to reduce the kinetic energy of P^{32} recoils from the (n,γ) reaction and thus to limit the probability of high-energy processes leading to re-entry into the parent molecule (*116*). Under these conditions the yields of $(CH_3)_3P^{32}$, $(CH_3)_2P^{32}H$, and $CH_3P^{32}H_2$ were 0.04–0.1%, 0.02–0.1% and 0.2–0.3% respectively. This result indicates an almost complete rupture of P-CH_3 bonds in the (n,γ) reaction.

An interesting approach to the problem of estimating the proportion of nuclear events which fail to rupture bonds has been made by Iyer and Martin in the case of the (n,γ) reaction in alkyl iodides (*139*). These authors have labeled iodides with the 1.27×10^7 year I^{129} isotope, and then studied the consequences of the $I^{129}(n,\gamma)I^{130}$ reaction. Mixtures of CH_3I and n-C_3H_7I have been prepared in which the I^{129} isotope was present as CH_3I or n-C_3H_7I or I_2. Assuming that the probability of I^{130} being retained by secondary re-entry processes in one of the two alkyl iodides is proportional to the mole fraction of that iodide, and that a given fraction of events fails to result in bond rupture, a set of simultaneous equations can be set up to predict the specific activities in the irradiated compounds. By this means it has been found that in liquid CH_3I and n-C_3H_7I failure to rupture bonds occurs in about 4% of cases. This is significantly greater than the values of 1.09 and 0.66% in the gas phase experiments of Table II, and suggests some recombination of the I^{130} atom with the radical formed by bond rupture within the initial cage of solvent molecules, or radiation-induced effects.

D. Bond Rupture by Charging Processes

After ejection of an inner electron by one of the processes described in Section I,A,*2* an Auger cascade may cause bond rupture. Bonding electrons may be lost, or Coulomb repulsion between charged regions of the molecule may cause dissociation.

The line widths observed for X-ray fluorescence and X-ray absorption edges are of the order of 2–40 ev, so that from the relationship $\Delta E \cdot \Delta t = \hbar$, the duration of the Auger cascade is 10^{-15}–10^{-16} sec (*28, 61, 241, 242, 312*). Molecular vibration periods are of the order of 10^{-14} sec, so that molecules will remain intact until the charge on the activated constituent atom has been fully developed by the Auger process. When the cascade has ended, charge will tend to be distributed over the rest of the molecule. In the case of the cascade initiated by $\mathrm{Br^{80m}} \rightarrow \mathrm{Br^{80}} + h\nu$ in $\mathrm{CH_3Br^{80m}}$, Wexler and Anderson (*310, 312*) have obtained evidence that some charge distribution occurs before the molecule disintegrates. Using the mass spectrometer developed for examining the charged fragment spectrum from nuclear events in gases (*310, 312, 316*) these authors have shown that fragments such as $\mathrm{CH_3Br^+}$, $\mathrm{CH_3^+}$, and $\mathrm{C^+}$ are produced with a fairly high probability. Consequently in considering the mechanism of bond rupture by Auger cascades repulsion between charged regions of the molecule must be taken into account.

The Auger effect can be treated either as a radiationless transition, involving electron-electron interaction in the shells, or as a process of successive X-radiation emission and internal conversion (*28*). In either case the probability is highest for ejection of the electron nearest to the vacancy. At the beginning of the cascade this probability is highest for ejection of electrons from the atom in which the initial vacancy has occurred, but as the cascade reaches the periphery, electrons from molecular orbitals may be involved. In the case where the charge builds up on an atom A in a molecule A(BCD . . .), and the ionization potential of the final state A^{Z+} exceeds the ionization potentials of B, C, or D, then charge redistribution can occur by electron transfer (*316*).

The potential energy of the system $\mathrm{A}^{Z+}(\mathrm{BCD})^{Y+}$ is:

$$V = \frac{(Ze)(Ye)}{r} \tag{4}$$

where r is the effective distance between the charge center of A^{Z+} and the charge center of $(\mathrm{BCD})^{Y+}$. The fragments A and BCD recoiling after bond rupture will have kinetic energies $V\,M_{\mathrm{BCD}}/(M_{\mathrm{A}} + M_{\mathrm{BCD}})$ and $V\,M_{\mathrm{A}}/(M_{\mathrm{A}} + M_{\mathrm{BCD}})$ respectively, where M_{A} and M_{BCD} are the fragment masses. After the Auger cascade in $\mathrm{CH_3Br^{80m}}$ Wexler and Anderson have found that the most probable fragments are $\mathrm{Br^{7+}}$ and $\mathrm{CH_3^+}$ (*312*). The total kinetic energy for this pair from Eq. (4) is 53 ev, considerably in excess of the C—Br bond energy of 2.3 ev. Bond rupture in this case would probably occur by simple loss of bond electrons, but in addition there is ample energy available for rupture from Coulomb repulsion.

E. BOND RUPTURE IN ISOMERIC TRANSITION

The chemical consequences of the isomeric transition $Br^{80} \rightarrow Br^{80m} + h\nu$ have been extensively studied in organic bromides. During the transition two gamma quanta are emitted in series, of energies 49 and 37 kev respectively (*287*). The energies of recoil from these quanta are 0.016 and 0.009 ev respectively, so that insufficient kinetic energy is available from this source for rupture of chemical bonds. The 49 kev step undergoes 100% internal conversion while the 37 kev step is converted in 55% of events (*246*). The conversion of the first step takes place with 84% probability in the K shell and 16% probability in the L shell. The corresponding figures for the second quantum are 87% K and 13% L. Auger cascades will be initiated by some of these conversions, while in other cases X-radiation will be emitted. Figure 2 shows the ion yields of charged bromine atoms from isomeric transition of Br^{80m} in CH_3Br^{80m}, as obtained by the method of charge spectrometry (*312*). The average charge is +6.2.

From Fig. 2 and the considerations advanced in Section II,D, it would be expected that bond rupture would be very extensive in the case of a molecule such as CH_3Br after isomeric transition. Since the daughter atom, Br^{80}, is itself beta-active its distribution can readily be followed in the reaction products. In view of the fact that the kinetic energy of the $CH_3^+ + Br^+$ couple from Coulomb repulsion would only be 7.6 ev, from Eq. (4),

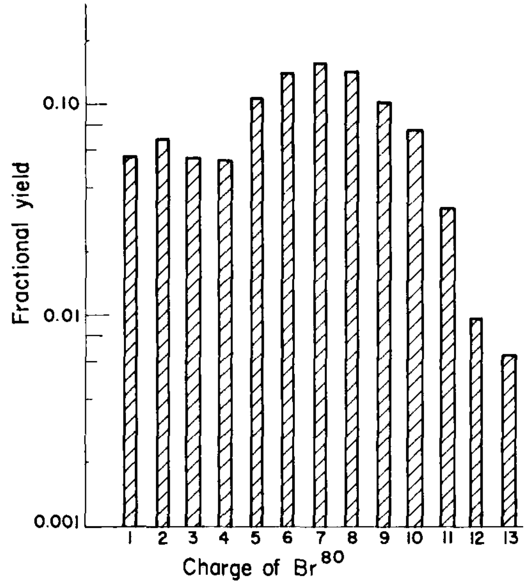


FIG. 2. Ion yields of charged bromine atoms from nuclear isomeric transition of Br^{80m} (*312*).

experiments to determine the absolute efficiency of bond rupture require to be done in the gas phase to avoid caging effects.

Table III shows the results of gas phase experiments on the dissociation of Br^{80m}-labeled organic bromides. From the table it emerges that the bond rupturing efficiency is very high. The discrepancy between results for HBr^{80m} and HBr^{80m} + allyl bromide (or α,β-dibromoethylene) as a scavenger for thermalized Br atoms (*104*, *120*) is not easily explained.

TABLE III

PROBABILITY OF BOND RUPTURE AFTER ISOMERIC TRANSITION IN GASEOUS Br^{80m}-LABELED BROMIDES

Gas phase constituents[a]	Probability of bond rupture (%)	Reference
HBr^{80m}	>95	(*104*)
HBr^{80m}(90) + $CHBr{=}CHBr$(2.3) + CH_3Br(5.4)	76	(*120*)
HBr^{80m}(91) + $CH_2{=}CHCH_2Br$(2.4) + CH_3Br(5.2)	76	(*120*)
DBr^{80m}(54) + $CHBr{=}CHBr$(1.4) + CH_3Br(3.1)	83	(*120*)
CH_3Br^{80m}(120) + HBr(60)	100	(*119*, *120*)
CH_3Br^{80m}(150) + HBr(0)	94	(*119*, *120*)
CH_3Br^{80m}(45) + HBr(45)	99	(*119*, *120*)
CH_3Br^{80m} + Br_2	94.4	(*50*)
CH_3Br^{80m} + Br_2	98.7	(*104*)
$C_2H_5Br^{80m}$ + Br_2	96.9	(*104*)
CCl_3Br^{80m} + Br_2	98.0	(*104*)
CCl_3Br^{80m} + Br_2	92.9	(*50*)
CF_3Br^{80m} + Br_2	99.0	(*50*)

[a] Figures in parentheses denote gas pressures in mm Hg.

Magee and Gurnee (*195*) have considered the implications of the experiments with allyl bromide or dibromoethylene (*120*), which seem to indicate that 17–24% of HBr or DBr molecules can survive isomeric transition, while in organic bromides this is not the case. For molecular survival to occur the bonds must remain intact during both the charging and discharging processes. Magee and Gurnee have selected likely charge states induced by the Auger cascade. From these states potential energy curves have been drawn up for the "homopolar" $(HBr)^{Z+}$ and polar $(H^+Br^{(Z-1)+})$ components of the Z^+ state. They find that for the sequence $Z(0\text{–}4+)$ there is a remarkable stability of both the homopolar bond dissociation energy and the bond distance with respect to the value of Z and the position of the missing electrons. The Coulombic repulsion curves for the polar component intersect the homopolar curves, but for $Z + 4$ the intersection occurs sufficiently far out to leave a potential minimum, i.e., a stable bond, unless direct transitions to excited states are involved. In the case of a molecule such as CH_3Br it is found that due to the lower ionization potential of CH_3 (9.96 ev) by comparison with H (13.6 ev) the polar repulsion curves pass through the homopolar attractive minima and lead to bond rupture.

Wexler and Anderson (*312*) have used charge spectrometry to determine the distribution of positively charged fragments from isomeric transition in CH_3Br^{80m}. The accuracy of measurements in the spectrometer is limited by virtue of the fact that according to Eq. (4) the different charged fragments will attain different kinetic energies, and that mass spectrometers have differing discriminations against fragments of differing initial kinetic energies. In the fragment spectrum $(CH_3Br^{80})^+$ occurs with a probability of 9.5–10%. This suggests that ejection of only one conversion electron does not necessarily lead to bond rupture. In those isomeric transitions in which the 49 kev quantum is converted and this step is followed only by X-ray emission together with radiation of the 37 kev quantum, the CH_3Br^{80} daughter will have a single positive charge. Such an ion evidently remains intact in ~10% of events, even though it may have been initially produced in a further fraction of events and undergone dissociation. The absence of $(CH_3Br^{80})^{2+}$ and $(CH_3Br^{80})^{3+}$ shows that multiply charged methyl bromide ions must dissociate. If the peripheral charge on the Br^{80} is greater than +1, then charge distribution over the whole molecule will occur by the charge transfer process outlined in Section II,D, since the ionization potential of $CH_3\cdot$ (9.96 ev) is always less than that of singly or multiply charged bromine (first ionization potential 11.84 ev). The CH_3^+ fragment is the most common in the spectrum, and this suggests that after the electron transfer process has removed one electron from CH_3 to Br^{Z+}, the molecule dissociates by Coulomb repulsion. Even in the case of $CH_3^+ + Br^+$ Eq. (4) yields 7.6 ev, considerably in excess of the C—Br bond energy of 2.3 ev. The appearance of C^{2+} and C^{3+} with small probabilities in the fragment spectrum suggests that in less frequent occurrences there may be intramolecular transfers of more than one electron.

F. BOND RUPTURE IN BETA DECAY

Molecules may be disrupted after beta decay of a constituent atom as a result of acquisition of recoil energy by the emitting atom, or as a result of electronic excitation or ionization by one of the processes described in Sections I,A,*2* and I,A,*3*.

Early studies on the chemical effects of β^- emission showed that in the $La^{143} \rightarrow Ce^{143} + \beta^-$ transition the Ce daughter in most cases was oxidized by one unit (*27*, *69*). Wexler (*308*) showed that the average charge on H^3H, $C^{14}O_2$, and A^{41} after β^- decay was approximately 1+.

Studies of bond rupture in the beta decay of $Pb^{210}(CH_3)_4$ using the fact that the daugher Bi^{210} is radioactive, demonstrated that about 80% of molecules survived the transition in the gas phase at 10 mm Hg pressure (*74*), despite the fact that emission of the beta particle is in this case followed by gamma decay with a high conversion probability. The maximum recoil energies from beta emission (0.006 ev) and ejection of the conversion electrons (0.12 ev) could not have led to bond rupture, but electronic excitation or ionization might have been expected to do so. More recent studies (*15*) indicate the relatively high stability of the $Bi(CH_3)_4^+$ formed as the initial product in the beta decay.

The chemical consequences of the beta-gamma decay $Te^{131} \rightarrow I^{131}$ have been studied in solutions of dibenzyl telluride in benzene and in the solid telluride (*117*). In the solid phase the Te—C bond was ruptured in at least 98.2% of the nuclear events as shown by the measured I^{131} retention in benzyl iodide. Assuming isotropic beta-neutrino emission 41.4% of the I^{131} atoms should have a kinetic energy of recoil of only 1.89 ev, and the hardest gamma quantum should have imparted a recoil energy of only 1.42 ev. Charge or electronic excitation effects due to shake-off or internal conversion probably account for the high percentage of bond rupture even in the presence of a cage of surrounding molecules.

The consequences of the $C^{14} \rightarrow N^{14} + \beta^-$ decay have been studied in ethane by preparing $C^{14}H_3C^{14}H_3$, the radioactivity of one of the carbons serving to trace the species resulting from beta decay in the other (*332*). In 47% of nuclear transformations $C^{14}H_3NH_2$ was obtained, i.e., the C—N bonds had not been ruptured. From Eq. (3), 59% of the kinetic energy of recoil from beta emission will be available to activate the C—N bond. The bond energy is 2.1 ev, so that only recoils with an energy greater than 3.6 ev should rupture the bond. Comparison of this value with the recoil spectra calculated for C^{14} with various assumed beta-neutrino interactions showed that ~74% of recoils have energy less than this value. Some cases of the observed bond rupture must therefore have been due to electronic excitation. Wolfsberg (*336*) has made a quantum mechanical calculation of the contribution of excitation to bond rupture, taking the lower limit for nondissociation to be the probability of a $1s^22s2p^3$ C atom becoming a $1s^22s2p^3$ positive N atom. This probability is found to be 0.815, so that on multiplying this by the 0.74 probability of failure to rupture bonds by recoil, the rough figure of 60% is found for the chance of molecular survival, in comparison with the observed figure of 47%.

The technique of charge spectrometry, mentioned in previous sections, has allowed a better appreciation of several aspects of molecular disruption by beta decay. Use of low gas pressures allows the primary products of molecular disintegration to be studied, free from collision-induced secondary reactions, while the mass-spectrometric technique allows detection and measurement of the charge, mass and relative abundances of the molecular fragments.

Fragmentation spectra of molecules disrupted by the beta decay of H^3 have been obtained (*310, 313, 316*).

Study of the decay of tritio-ethane shows that $H^3 \rightarrow He^3 + \beta^-$ invariably results in disruption of the C—He bond. The He^3 always comes off as a neutral atom, the positive charge being taken by the organic fragment. The fragment $(C_2H_5)^+$ is dominant, constituting ~80% of the ion beam. In the remaining 20% of cases this "initial fragment" acquires sufficient excitation energy to dissociate further. Since $(C_2H_4)^+$, $(C_2H_3)^+$, $(C_2H_2)^+$, $(C_2H)^+$ and $(C_2)^+$ are found, the initial fragment can presumably dissociate

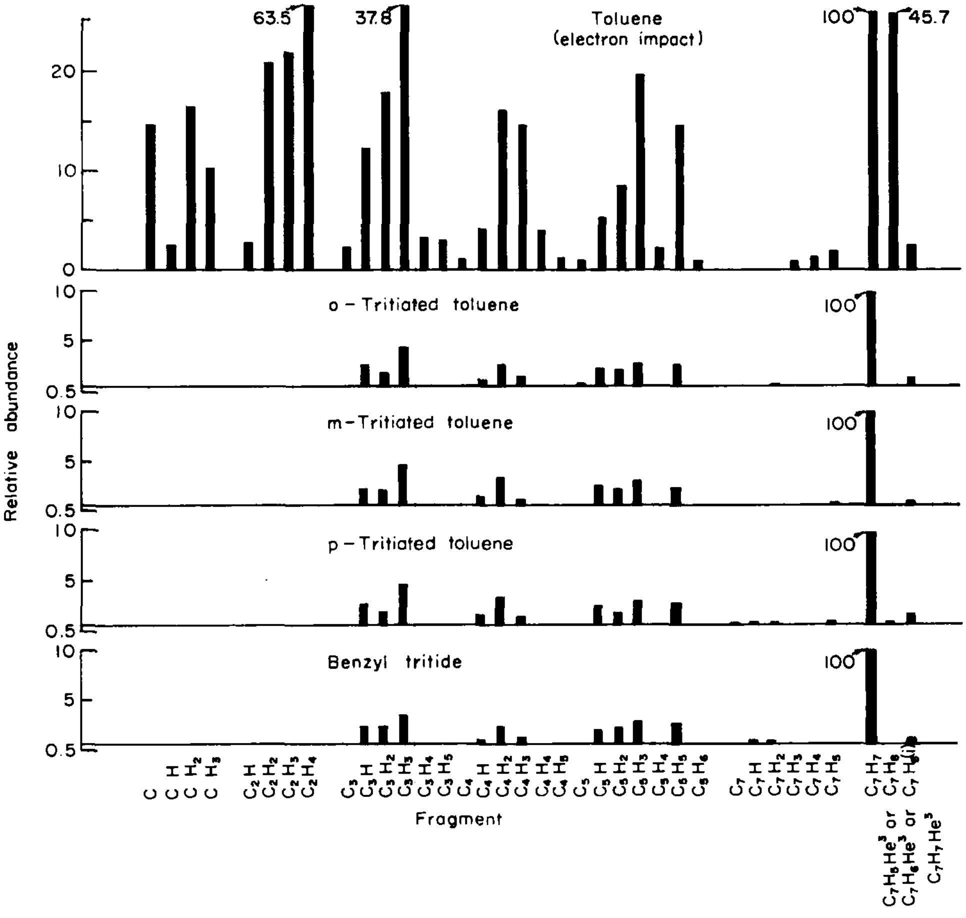


Fig. 3. Comparison of fragment ion yields from beta decay of mono-tritiated toluenes and from electron impact on nonradioactive toluene (*313*).

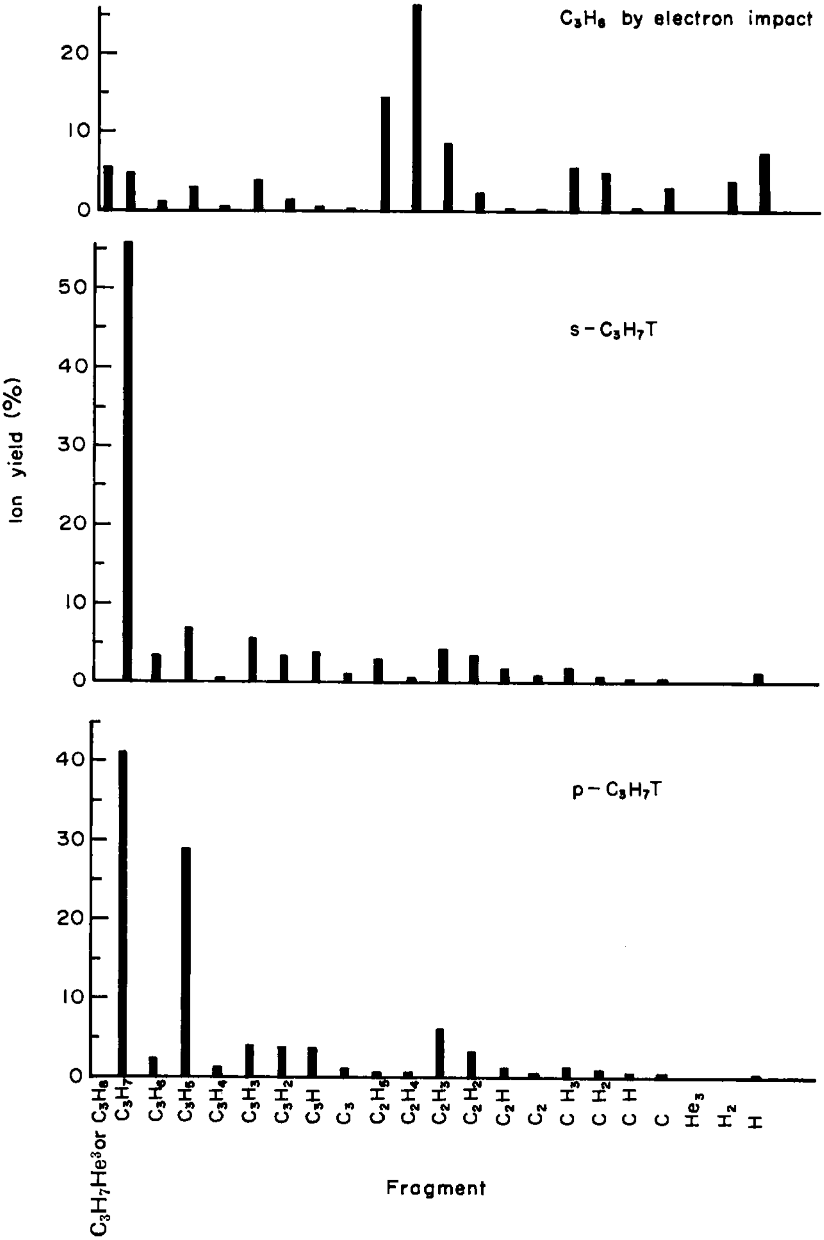


FIG. 4. Comparison of fragment ion yields from beta decay of mono-tritiated propanes and from electron impact on nonradioactive propane (*313*).

by loss of neutral atomic and molecular hydrogen. H^+ is not present in the spectrum to any significant degree.

Charge spectrometry has allowed some information to be obtained as to the influence of the position of the H^3 in a polyatomic molecule on the mode of disintegration (*313*). Fragmentation spectra have been obtained from primary and secondary mono-tritiated propane and from *ortho-*, *meta-*, *para-*, and *alpha*-monotritiated toluene, and are shown in Figs. 3 and 4. Similar general characteristics to those given for $C_2H_5H^3$ decay in the previous paragraph are found, but in addition certain specific features are present in the propane-toluene decay systems. The abundances of most of the singly charged fragments found from decay in propane are independent of the isomeric state of the compound. Exceptions to this are the fragments $(C_3H_7)^+$, $(C_3H_5)^+$, $(C_2H_5)^+$ and H^+. The mass spectra for the four H^3-toluenes are very similar, so that the mode of molecular disintegration in this case is largely independent of the position of the tritium in the molecule.

TABLE IV

YIELDS OF INITIAL FRAGMENT IONS FROM TRITIATED ORGANIC COMPOUNDS (*310*)

Molecule	Initial fragment ion	Ion yield %	Reference
CH_3H^3	CH_3^+	83	(*275*)
$C_2H_5H^3$	$C_2H_5^+$	80	(*316*)
p-$C_3H_7H^3$	$C_3H_7^+$	41	(*313*)
s-$C_3H_7H^3$	$C_3H_7^+$	56	(*313*)
$C_6H_5H^3$	$C_6H_5^+$	72	(*44*)
o-$C_6H_4H^3CH_3$	$C_7H_7^+$	78	(*313*)
m-$C_6H_4H^3CH_3$	$C_7H_7^+$	79	(*313*)
p-$C_6H_4H^3CH_3$	$C_7H_7^+$	76	(*313*)
$C_6H_5CH_2H^3$	$C_7H_7^+$	79	(*313*)

In endeavoring to interpret the results of beta fragmentation spectra it should first be pointed out that after beta emission involving no secondary electron ejection the daughter atom should bear a single positive charge. In fact +1 states predominate in the spectra, +2 ions occurring with a very low probability. The theoretical treatments of Migdal (*199*) and Levinger (*170*) show that any ionization initiated by beta emission occurs with highest probability in the outermost shells, so that bonding electrons of the excited atom are most likely to be affected. In all fragment spectra from H^3 decay in polyatomic molecules so far studied the daughter molecule ions formed directly by the transition are absent, while the yields of ions formed by splitting off neutral He^3 are high (*310*). The yields of such ions are shown in Table IV. In Section I,A,*3* it was pointed out that on theoretical grounds 67–70% of the $(He_3)^+$ ions should be formed in the ground state. In these cases one might expect the weak He^3—C bond to rupture, but the initial fragment ions would have no energy capable of causing their further dissociation. The theoretical yield of initial ions thus predicted is in reasonable agreement with the values of Table IV. The apparent exceptions in the case of $C_3H_7^+$ are possibly due to the fact that the energy for H_2 removal is relatively lower for these ions than for others in the table (*310, 313, 316*). Transitions to low-lying energy states consequent upon beta emission may thus have been able to effect $C_3H_7^+ \rightarrow C_3H_5^+ + H_2$. The total yields of $C_3H_7^+ + C_3H_5^+$ may thus more accurately represent the percentage of events in which the initial fragment ion has zero or small energy of electronic excitation, and these total yields are 70% for n-$C_3H_7H^3$ and 63% for s-$C_3H_7H^3$, more nearly in accord with the remaining yields in the table.

It is desirable to find an explanation for the distribution of products resulting from further decomposition of the initial ion in the 20–30% of events in which sufficient electronic excitation has been imparted to it. To solve this problem Wexler and Hess (*316*) have applied the theory developed for the statistical treatment of mass spectra obtained from polyatomic molecules by electron impact. Rosenstock *et al.* (*245*) have proposed that after ionization by electron impact the molecule-ion possesses electronic and vibrational excitation energy. Decomposition does not occur until after several vibration periods, during which time a radiationless redistribution of energy amongst the various degrees of freedom can occur in random fashion with high probability. The molecule-ion then decomposes into ionized and neutral fragments when the nuclei are in the proper configuration and a sufficient amount of vibrational energy has concentrated in the necessary degrees of freedom.

In the case of H^3 decay in organic molecules it is considered that the He^3—C bond is disrupted in a single vibration, since in the Franck-Condon transition the vibrational energy of the product ion exceeds the weak C—He^3 binding energy. In those cases in which the beta emission leads to higher states, the electronic excitation energy is randomly distributed over the initial ion, and step-wise dissociation of the ion occurs. The idea of randomization of energy is favored by the similarity of the dissociation spectra for the two H^3-propanes and for the four H^3-toluenes shown in Figs. 3 and 4. The application of statistical mass spectrum treatment is to some extent justified by the fact, shown in Fig. 3, that the types of ionic fragment are the same in both cases.

To test the applicability of the statistical treatment it is interesting to compare beta decay spectra with those obtained from molecular dissociation in charge transfer reactions (*47, 48, 150, 160, 173, 174, 296*). An advantage of the charge transfer technique is that the activation energy is known and is equal to the recombination energy of the ion minus the ionization potential of the molecule, whereas in the electron impact studies the excitation energy supplied cannot be exactly determined. Table V shows considerable differences in patterns of molecular dissociation from the three different modes of activation. C—C bond rupture is more frequent in both electron impact and charge transfer dissociation than in beta decay, as shown by the relatively enhanced yields of C_2 and C ions in the first two processes. Čermák and Herman (*47*) quote data obtained by Chupka and Kaminsky for electron impact in propane which agree well with the charge transfer dissociation spectra of Table V, after appropriate normalization of the energy axis. From this agreement they conclude that the fragmentation mechanism of excited polyatomic ions may be independent of the way in which excitation energy is supplied. The data for propane, however, seem to indicate some differences for activation by beta decay.

TABLE V

ION YIELDS FROM H^3 DECAY, ELECTRON IMPACT AND CHARGE TRANSFER DISSOCIATION IN PROPANE GAS

	% Ion yield						
				Molecular dissociation from charge transfer with energies[b]			
Ion	H^3 decay in p-$C_3H_7H^3$ [a]	H^3 decay in s-$C_3H_7H^3$ [a]	Impact of 150-volt electrons[a]	1.3 ev	3.2 ev	4.7 ev	10.4 ev
$C_3H_8^+$	<0.2	<0.2	6	0	0	0	0
$C_3H_7^+$	41	56	5	39	24	0	0
$C_3H_6^+$	2.2	3.4	1	7	6	0	0
$C_3H_5^+$	29	7	3	0	9	15	12
$C_3H_3^+$	4.0	5.3	4	0	0	0	38
$C_2H_5^+$	0.6	2.9	14	29	54	12	0
$C_2H_4^+$	0.5	0.7	27	22	9	8	0
$C_2H_3^+$	6.0	4.3	9	0	0	54	38
$C_2H_2^+$	3.2	3.6	2	0	0	9	8
CH_3^+	1.2	1.7	5	0	0	0	10

[a] Ref. (*313*).

[b] From figures in ref. (*47*).

In the case of decomposition of toluene a somewhat different situation prevails. Impact of 50-volt electrons yields a rather different fragmentation spectrum from that obtained in beta decay, as shown in Fig. 4. The aromatic ring structure seems to be more resistant to decomposition by beta decay than by electron impact. Nevertheless, mass spectra from electron impact in mono-deuterated toluenes obtained by Meyerson and Rylander

(*198, 254, 255*) are rather similar to those from activation by beta decay. It has been suggested (*255, 310, 313*) that excited tolyl or benzyl ions from both modes of activation expand to form the 7-membered tropylium ring ion, which is the common precursor of all the observed fragments. A few differences are observed, however, in the benzyl tritide pattern, suggesting that the tropylium ion may not be the only pathway of decomposition.

Similar studies have been done using the $Br^{82} \rightarrow Kr^{82} + \beta^-$ decay in 1,2-$C_2H_4BrBr^{82}$ and CCl_3Br^{82} (*309, 310*). The fragmentation spectra have the same general characteristics as those from H^3 decay. The C—Kr^{82} bond invariably breaks after the transition, leaving a positively charged initial ion which decomposes in some 30–35% of events.

From the ion yields after beta decay it is possible to estimate the distribution of excitation energy in the excited daughter molecular ion (*310, 313*). The quasi-equilibrium theory of molecular dissociation (*245*) is applied. The excited molecular ion is considered to dissociate by successive, competing, unimolecular reactions. Energetically plausible decomposition sequences of the type shown in Fig. 5 are constructed on the basis that energy of activation from electron impact appearance potentials (*92*) must be equal to or greater than the heat of each particular unimolecular decomposition, aided by the observed presence of metastable ions in electron impact mass spectra. Supporting evidence for the validity of a scheme, such as that of Fig. 5, in which decomposition proceeds mainly by H_2 elimination, comes from electron impact studies (*56*). A histogram of the type shown in Fig. 6 can now be constructed in which the area under each rectangle is proportional to the experimental ion yield. The energy limits

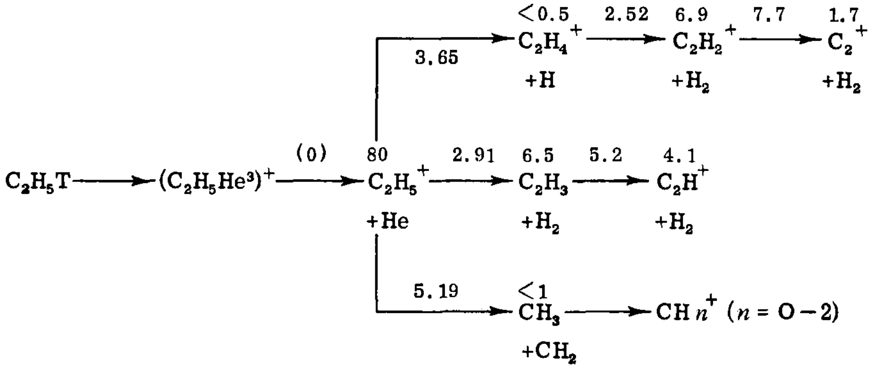


FIG. 5. A proposed mechanism for the formation of the mass spectrum from beta decay in $C_2H_5H^3$ (*310*). The numbers above the fragments refer to the observed relative percentage abundances. The numbers above the arrows indicate, in electron volts, the minimum energies required for the various decompositions. The reaction $(C_2H_5He^3)^+ \rightarrow C_2H_5^+ + He^3$ is assumed to require no activation energy.

for each ion are set by the differences between the appearance potentials of the particular ion and its daughter ion and the appearance potential of the parent ion in the sequence. The integral curve from the histogram yields the energy distribution from beta decay.

For beta decay in *s*-$C_3H_7H^3$ the energy distribution is found to be heavily weighted towards the lower energy values, 56% of the $(C_3H_7He^3)^+$ being formed with less than 2.1 ev (*313*). Above 2 ev the distribution is fairly flat tailing off to zero at about 18 ev. A similar distribution is obtained for mono-tritiated ethane (*313, 316*).

Comparison of the energy distributions thus found for the decay process with those quoted in Section I,A,*3* from the theoretical treatments of Migdal and Winther shows reasonable agreement. Theory predicts that 67–70% of the beta decays should yield zero excitation energies, while 25% of the He^3 daughters should have energies less than 20.5 ev. Experiment in the case of tritio-*s*-propane yields 56% of $(C_3H_7He^3)^+$ with energies less than 2.1 ev and a high energy limit of ~18 ev, while in the case of tritioethane 80% of the $(C_2H_5)^+$ have less than ~3.7 ev and the high energy limit is ~16 ev.

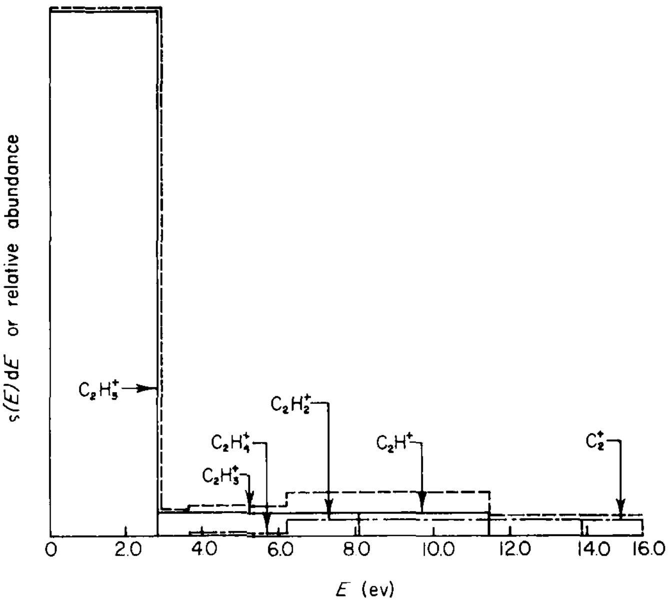


FIG. 6. Empirical breakdown histogram showing the derived distribution $p(E)dE$ of excitation energies in $(C_2H_5He^3)^+$ daughter ions following beta emission (*310*).

Beta decay effects have also been studied in tritium hydride (*281, 311*). The observed ion yields are $(He^3H)^+$, 89.5–93.2%; $(He^3)^+$, 5.1–8.2%; H^+, 1.6–2.3%; $(He^3)^{2+}$, 0.14%. A marked difference from tritium decay in organic molecules is the strong tendency for $(He^3H)^+$ to remain bound, at least for the $\sim 10^{-4}$ sec ion transit time in the spectrometer. Ion disruption can then occur by:

$$(He^3H)^+ \rightarrow (He^3)^+ + H \tag{5}$$

$$(He^3H)^+ \rightarrow He^3 + H^+ \tag{6}$$

Since the $(He^3)^+$ yield is greater than H^+ there is a predominance of the reaction which involves one electron of the bond going to each fragment.

In considering the disruption of a diatomic molecule it must be remembered that the beta particle is emitted in a time which is very short by comparison with the periods of electronic and atomic motion, so that only vertical Franck-Condon transitions occur. Molecular dissociation will occur whenever the transition achieves a vibrational level higher than the dissociation limit of a bound daughter, or when a repulsive daughter state results, or when predissociative transitions can occur. The observed ion yield of 90% for $(He^3H)^+$ suggests that the bulk of the transitions are to the $(He^3H)^+$ ground state, and that most excited levels reached by the transfer of energy from the beta particle, or by subsequent radiation, are also attractive. Using the time-dependent sudden perturbation theory Cantwell (*38*) has calculated that the probability of transitions from the ground level of H^3H to the ground state of $(He^3H)^+$ is 58%, and of these cases, 55% are to the three lowest vibrational levels which should be well below the dissociation limit.

Something must also be said about the role of kinetic energy of recoil in bond rupture by beta decay. The simplest case for discussion of this point is the diatomic molecule H^3H. The maximum beta energy of H^3 is 0.018 Mev so that from the formula given in Section I,A,*1* the maximum recoil energy is 3.4 ev, and from Eq. (3) the bond activation energy will be 0.85 ev. The dissociation energy of $(He^4H)^+$ is 1.75–2.05 ev (*85*), and therefore even the maximum available recoil energy will not dissociate the initial ion in its ground state (*311*). In addition, from the observed spectrum of H^3 beta rays it can be calculated that 92% of the recoils have $E_r < 2.0$ ev, so that $E_i > 0.5$ ev.

Although recoil energy thus plays a negligible part in decomposing $(He^3H)^+$ in its ground state the possibility must be remembered that initial ions formed on sufficiently high vibrational levels may be induced by recoil to dissociate. In the case of the tritio-organic molecules referred to earlier in this section, Eq. (3) shows that almost all the recoil energy is available for bond rupture. If the C—He^3 bond were ruptured due to recoil energy alone, this would imply that the bond energy is very small since this bond is ruptured in virtually all cases and it can be calculated from the H^3 beta ray spectrum that 8% of recoils have energies less than 0.18 ev.

III. Formation of Chemical Bonds by Atoms Activated by Nuclear Transformation

A. GENERAL CONSIDERATIONS

Some of the earliest studies of the chemical effects of nuclear transformation in organic halides led to a comparison of the yields of organically bound radioactive atoms in gas, liquid and solid phases (*319*). These yields have commonly been called the "organic retention." Retention was usually in the range 0–10% for gases, as shown in Table II. In solids or liquids retentions were usually in the range ~20–90%. It was concluded that in the case of gas phase studies the frequency of primary bond rupture by the nuclear process was being observed, whereas in liquids or solids the initially freed radioactive atom was re-entering into organic combination (secondary retention).

Several models were advanced to account for secondary retention. These models have been well reviewed elsewhere (*31*, *66*, *124*, *319*) so that here only a brief account will be given of the features particularly significant for gases and liquids. Harbottle and Sutin (*124*) and Yankwich (*399*) have discussed the implications of the models for recoil reactions in solids.

The elastic-collision "billiard-ball" model proposed by Libby (*172*) assumes that a recoiling atom, with kinetic energy considerably greater than bond energies, frees itself from its parent molecule and then loses its excess energy predominantly by elastic collisions with atoms of its environment. In nearly head-on collisions with atoms of similar mass most of the kinetic energy can be transferred to the struck atom, which may be dislodged from its chemical bonds. If the recoil is left with kinetic energy below a certain critical value necessary for escape from the collision site, bond formation will occur between the recoil and the molecular residue. At kinetic energies exceeding ~20 ev the energy of the incident atom is very much greater than the energies of bonds within the struck molecule, and the effective duration of the collision is very much less than the time required for intramolecular vibrational relaxation, so that energy from the collision is inefficiently transmitted along the bonds. Thus the "hot" recoil strikes a molecule which can be regarded as a loosely coupled collection of atoms.

This model has been developed further by Miller, Gryder, and Dodson (*201*), and by Capron and Oshima (*42*). The model predicts that in solids the cage of molecules surrounding the collision site would oppose escape of the suddenly cooled recoil, thus favoring high organic retention, whereas absence of such a cage in gases should give low retentions, as observed. Willard (*319*) has reviewed the extensive evidence bearing out these predictions in gas, liquid, and solid phase irradiations of organic halides with neutrons.

Epithermal reaction schemes were proposed as modifications to the billiard-ball model by Libby (*172*) and Miller and Dodson (*200*). It is found that nuclear activation can lead to reactions not efficiently initiated by thermal or photochemical means (see, e.g., *200* together with *243*), and this suggests that some of the atoms recoiling from nuclear transformation enter into organic combination during the energy-loss process before thermalization. The reaction mechanism of Miller and Dodson focuses attention on the epithermal energy range of a few ev, in which the recoil can form an excited complex with an organic molecule, which then decomposes into various products incorporating the radioactive atom (*200*). Alternatively, in the "strong coupling" epithermal model, after cooling by collisions to ~10 ev, the recoil can undergo inelastic collisions in which it imparts energy to the struck molecule as a whole (*66*, *93*, *172*). Vibrational excitation of the molecule may then lead to dissociation into fragments which can combine with the radioactive recoil. These models account for the fact that the radioactive atom is found in molecules other than those of the parent type (see Section III,B,*2*), and for the fact that solutions of elementary halogens or arsenic in hydrocarbons yield organically bound radioactive atoms on neutron irradiation (*37*, *125*, *178*, *236*, *273*, *319*). Like the billiard-ball mechanism the epithermal reaction models can predict a phase effect, since a cage of adjacent molecules may act to hold the recoil in close contact with the fragments of the molecule disintegrated by the inelastic collision.

The billiard-ball and epithermal models involve "hot" highly localized reactions which should not be influenced by low concentrations of scavengers capable of removing thermalized free radicals. The observed effect of small amounts of such scavengers on organic retention (see Section III,B,*2*) has suggested to Willard (*319*) a process in which the thermalized recoil atom encounters by diffusion some of the radicals which it has produced by collision along its track, and then combines with them. The diffusion-dependent recombination processes will be scavenger-sensitive. This mechanism has been called the "brush-heap" or "random-fragmentation" model. It predicts a phase effect on the distribution of radioactive products in two ways. In the first place the relative probability of different types of bond rupture caused by the recoil in inelastic collisions will vary with the density and crystal structure of the medium. In the second place the phase conditions will influence the relative chances of diffusion of the various fragments away from the immediate vicinity of the thermalized recoil.

The models described above have been developed almost entirely from work on neutron-irradiated organic halides. It can be seen that they predict both "hot" reactions (billiard-ball and epithermal) and "thermal" reactions (brush-heap), a variety of products incorporating the recoil (epithermal and brush-heap) and definite phase effects (all three). Since the earlier work with organic halides the experimental basis has been considerably widened, particularly by the use of hot H^3 atoms and by work with polyvalent recoils, and the relative roles of these three mechanisms are now somewhat better understood. In addition, as will be seen, the work with H^3 recoils has suggested important revisions of the models described above.

Theoretical studies of the mechanisms involved in hot collisions have been commenced. Magee *et al.* (*194*, *207*) have examined the probability of dissociation of diatomic molecules induced by collision with an atom having a velocity in the range $\sim 10^6$–$\sim 10^8$ cm/sec, for which the collision is adiabatic with respect to electronic state but non-adiabatic with respect to vibrational and rotational state. In a hot collision the energy is large by comparison with the binding energy of the molecule, so that the only region of the interaction curve for which the potential energy is as large as the total energy is that for which the nucleus of the incident atom approaches very closely to one of the nuclei of the molecule. In such a region the potential energy of the system arises almost exclusively from the interaction of the atoms which are close together, so that a reasonable approximation is to treat the potential energy of the system as a sum of terms arising from individual interactions between pairs of atoms. It is found for the HBr molecule that the curve for an r^{-2} potential reasonably approximates to the curve based on the Seitz interaction potential (*266*). The r^{-2} potential is also to some extent justified by range-energy relationships observed for recoils (*194*), and has been adopted in calculations of bond rupture probability as a considerable advance on the billiard-ball potential, which is 0 for $r \geqslant r_0$, and ∞ for $r < r_0$. Curves of the probability of dissociation of HBr, $P_D(\Delta E)$, have been derived as a function of the energy, ΔE, transferred to the HBr molecule in a hot collision with H or Br atoms (*194*). It should, however, be borne in mind that the approximation of deriving the potential energy for the whole collision system from individual pair-interactions will be reasonably valid in the high energy region, but will lose validity with decrease in energy, and will be less valid for collisions in which there is a small angle between the momentum impulse of the struck atom and the direction of its bond to the rest of the molecule.

B. Hot Reactions Resulting from Nuclear Activation

Hot reactions may be expected to have some of the following characteristics (*322*):

(a) They may yield products not formed by thermal reactions.
(b) They should be temperature independent.

(c) They should not be affected by low concentrations of radical scavengers.
(d) They may be influenced by adding inert additives that remove the kinetic, vibrational or electronic energy of the activated species before it undergoes a retention-causing collision.

1. Hot Reactions in the Gas Phase

Hot reactions have been demonstrated in gas-phase studies of halogens activated by neutron capture. The reaction $I^{127}(n,\gamma)I^{128}$ in gaseous CH_4 gives 43–51% I^{128} as CH_3I^{128} (*136*). In this case billiard-ball collisions as originally conceived are ruled out since only I-C and I-H collisions can occur. Two possibilities have been suggested for the retention-causing mechanism. In the first case the iodine could react by imparting sufficient of its kinetic energy of recoil to the I^{128}-CH_4 complex to overcome the endothermicity of the reaction. In the second case internal conversion of the (n,γ) quanta could impart a positive charge to the I^{128} (*314*). During neutralization of this charge the I^{128} could acquire energy of electronic excitation, as mentioned in Section I,A,*3*, and the excited I^{128} could then react with CH_4. The various displacement and abstraction reactions by which I or I^+ can react with methane are endothermic by amounts varying from 0.78 to 4.98 ev. For the kinetic energy mechanism Eq. (3) requires that the iodine atom or ion should have an energy $(128 + 16)/16 = 9$ times the endothermic energy of the reaction, i.e., in the range ~7–35 ev. Clearly such an energy would be available in a considerable percentage of the nuclear events, since the maximum recoil energy from $I^{127}(n,\gamma)I^{128}$ is 182 ev, corresponding to emission of a single quantum.

An attempt has been made to discriminate between the above two mechanisms by adding inert gas moderators to remove the I^{128} kinetic energy before it collides with CH_4, and by adding gases which have lower ionization potentials than atomic iodine to remove the I^{128} charge before collision with CH_4 (*169*). He, A, and Xe moderators reduce the CH_3I^{128} yield. The number of collisions necessary to reduce the I^{128} recoil energy from its maximum value to thermal energies can be calculated from collision theory. The probabilities that I^{128} recoil energy will be reduced below the threshold for a retention-causing reaction are found to be greater than the fractional reductions in retention, suggesting that the kinetic energy mechanism is not entirely responsible for retention. Gases such as I_2, CH_3I, C_2H_5I, C_3H_7I, and NO, which have lower ionization potentials than I, were in general more effective than the inert gases in lowering CH_3I^{128} yield, suggesting that the mechanism based on the I^{128} charge must play some part. Further studies have shown that large excesses of inert gas moderator cannot completely suppress the retention (*237*).

When the curves of organic I^{128} yield versus mole fraction additive are extrapolated to unit mole fraction additive in the case of neutron irradiated $I_2 + CH_4$, it is found that the organic yield is 36% in the case of Ne, A, and Kr additives but only 11% in the case of Xe additive (*237*). The retention of I^{127} in organic combination in the absence of any additive is 54%. It is considered that the reduction of organic yield from 54 to 36% is the result of removal of excess kinetic energy by the inert gas moderator. The additional reduction from 36 to 11% observed in the case of xenon is not likely to be due to quenching of I^{128} excited states, since inert gases are not effective quenching agents. It is more likely that the 25% drop in organic yield is due to charge transfer from the I^{128} to the xenon. The picture emerges of 18% of organic I^{128} resulting from hot reactions involving high kinetic energy, 25% resulting from $I^+(^1D_2) + CH_4$ reaction inhibited by xenon, and 11% resulting from reaction of CH_4 with I^{128} ions or highly excited atoms not quenched by xenon. When O_2, N_2, and CF_4 are added to $I_2 + CH_4$ mixtures before neutron irradiation, the organic yield curves extrapolate to 36%, so that these additives can only moderate the high kinetic energy reaction (*237a*). On the other hand C_2F_6 and CH_2F_2 reduce the organic yield to 11%, so that these gases can undergo charge transfer or perhaps competitive reaction with $I^{128+}(^1D_2)$. NO, CH_3I, CF_3I, $n\text{-}C_3H_7I$ and C_6H_6 reduce the organic yield to zero at unit mole fraction, and are thus capable of inhibiting all reactions of I^{128} with methane. The ionization potentials of these last additives are all less than that of the iodine atom, so that the 11% $I^{128} + CH_4$ reaction may be being inhibited by charge transfer with I^{128} ions. Alternatively the I^{128} ions may be being trapped in organic form by an exoergic charge transfer reaction of the type $I^+ + CH_3I \rightarrow I_2^+ + CH_3$.

In the case of the $Br^{79}(n,\gamma)Br^{80}$ reaction in methane the efficiency of inert gas moderators in lowering the organic retention increases in the order He, Ne, A, Kr, Xe, which is the order of increased energy transfer per Br^{80}-inert gas collision (*236*). Furthermore a plot of organic retention versus mole fraction CH_4 extrapolates to $0 \pm 2\%$ at zero mole fraction CH_4. In this system it seems that organically bound Br^{80} results mainly from the kinetic energy mechanism, a conclusion strengthened by the finding that Eq. (8) of the Estrup-Wolfgang theory described later is applicable.

Williams and Hamill (*325*) found that a certain percentage of HBr^{80} was formed as a result of the $Br^{79}(n,\gamma)Br^{80}$ reaction in gaseous $C_2H_5Br + C_2H_4 + HBr$, even at high ethylene pressures and suggested a hot gas phase reaction of the type:

$$Br^{80}\ (\text{hot}) + RH \rightarrow HBr^{80} + R \qquad (7)$$

Willard *et al.* (*103*, *136*, *169*) have pointed out, however, that it is generally difficult to separate the possibility of a hot gas phase reaction of this type from the possibility of ion-molecule reactions. In the case of the $Cl^{37}(n,\gamma)Cl^{38}$ reaction in gaseous n-C_4H_9Cl and n-C_3H_7Cl, with or without HCl, a fairly constant organic retention of 10–16% was found (*51*). The authors concluded that the observed constancy of retention irrespective of chain length indicated that the probability of collisions of the Cl^{38} with a chlorine atom, relative to the probability of collisions with other parts of the chain plays no part in the mechanism. They suggested that momentum-transfer properties were unimportant, and that an ion-molecule interaction probably occurred after internal conversion of the (n,γ) quanta. Ion molecule reactions of the type which could form organic halides have high velocity constants in the gas phase (*88*, *259*, *285*, *297*) and large charge-exchange cross-sections may be found consequent upon facilitated transition from kinetic to excitation energy (*296*).

Estrup and Wolfgang (*79*) have developed a kinetic theory of hot-atom reactions. These reactions differ from low-energy interactions, for which $K = pZ \exp(-\Delta E/RT)$, in that $E \gg \Delta E$, so that $\exp(-\Delta E/RT) \approx 1$. It emerges that in the high energy region p is not constant but energy dependent.

The Estrup-Wolfgang theory assumes that:

(a) the recoil loses energy in elastic collisions,
(b) the recoil has an initial energy, E_0, and that when the energy has been reduced by collisions into a range $E_2 - E_1$, retention-causing reactions can occur.
(c) $E_0 - E_2$ is sufficiently large for a number of collisions to have been made before the $E_2 - E_1$ range is reached, so that a statistically well-defined distribution of energies prevails within this range.
(d) $E_1 \gg$ thermal energies.

Applying usual theory for elastic collisions to the slowing down process (*97*, *306*) it is found that the radioactivity of a single product of hot reaction, A_i, can be related to the activity of all products of reaction, A_s, by the expression:

$$\frac{A_i}{A_s}\frac{\alpha}{f} \approx I_i - \frac{f}{\alpha}K_i. \tag{8}$$

In this equation α is the logarithmic energy decrement given for elastic collisions by:

$$\alpha = 1 - \frac{(M-m)^2}{2Mm}\ln\left[\frac{M+m}{M-m}\right] \tag{9}$$

where m is the mass of the hot atom, and M the mass of the struck molecule (*97*).

In Fig. (8), f is the relative probability of collisions between the hot atom and molecules capable of giving the product for which A_i is measured. I_i is an integral of the form:

$$I_i = \int_{E_1}^{E_2} \frac{p_i(E)}{E} dE \tag{10}$$

in which $p_i(E)$ is the energy-dependent collision efficiency with a type i compound. K_i is given by:

$$K_i = \int_{E_1}^{E_2} \frac{p_i(E)}{E} \int_{E}^{E_2} \frac{p(E)}{E} dE\, dE \tag{11}$$

Equation (8) can be used to test the validity of the theory. If the radioactivity of a single product can be determined, then a plot of $\alpha/f \times A_i/A_s$ against f/α should approximate to a straight line, at least for small values of f. If a straight line is obtained this yields some evidence that the reaction considered is a hot one.

Tests of this kind have been applied by Estrup and Wolfgang to products from the $He^3(n,p)H^3$ reaction in CH_4 with inert gas moderator (*79*, *80*). In previous work (*77*, *78*, *103*) it had been shown that HH^3, CH_3H^3, and $CH_2H^3\cdot$ are probably formed by hot reactions. Small amounts of radical and ion scavengers such as I_2 gas did not affect the yield of these products, whereas there was a marked depression of the HH^3 yield due to thermal abstraction of H from CH_4 or of the combination of thermalized H^3 with radiation-formed species to form higher tritiated hydrocarbons. The presence of excess helium reduced the yield of the hot products by acting as moderator (*77*). Altering the temperature during the irradiation did not affect the yield of hot products (*77*). Nitric oxide and oxygen could also be used as scavengers to test which of the products were formed by hot reaction (*161*, *247*).

Figure 7 shows that Eq. (8) does in fact apply to the activities of CH_3H^3 in the presence of inert gas moderators. Rack and Gordus (*236*) have applied the Estrup-Wolfgang theory to the total yield of organically retained Br^{80} after activation by neutron capture in CH_4 with inert gas moderators and have found evidence of a linear relationship between α/f [% Br^{80} as organic] and f/α within fairly large margins of error. Similar results were obtained with the $I^{127}(n,\gamma)I^{128}$ reaction in CH_4 (*237*).

It has been pointed out (*189*) that the Wolfgang-Estrup theory assumes energy loss by elastic collisions, an assumption valid for monatomic inert gas moderators in methane, but not necessarily applicable in other cases. It has been maintained (*331*) that the theory is not sensitive to the assumption of elastic collisions. In the regions of low moderator concentration and thus largely inelastic collisions the expressions are not sensitive to the col-

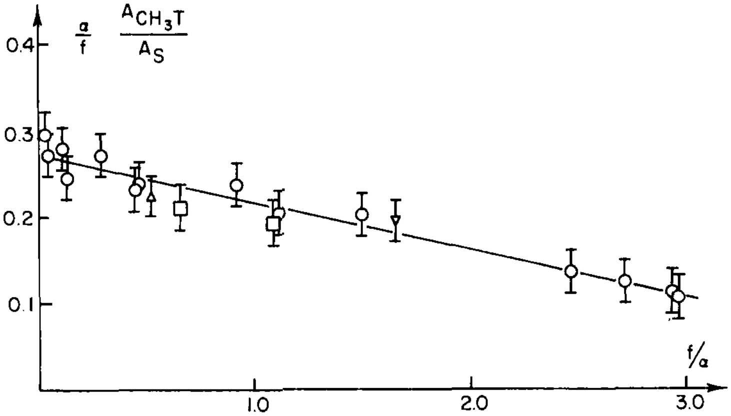


FIG. 7. Relationship between $(\alpha/f)(A_i/A_s)$ and f/α of Eq. (8) for H^3 recoils in methane with inert gas moderators (*79*).

lision parameter, α, while in the α-sensitive region of high moderator concentration the bulk of collisions will be elastic.

Gordus *et al.* (*102c*) have given a preliminary announcement of a hot atom reaction model based on the treatment developed by Miller *et al.* (*201*) to deal with high-energy reactions in binary liquid systems. The treatment of Gordus *et al.* allows direct calculation of the average reaction probability per energy increment, I of Eq. (10), from thermodynamic and transport property data, and can be adapted to include the effects of moderation by inert gases. The model apparently accounts successfully for the HH^3/DH^3 yield ratio for H^3 recoils in H_2-D_2 mixtures (*164*), the $A_{CD_3H^3}/A_s$ values for H^3 recoils in CD_4 with inert gas moderators (*66*), and the observed yields of various products of reaction of hot H^3, Br^{80} and I^{128} atoms with gaseous CH_4, C_2H_6, and C_3H_8.

Semiquantitative agreement has been obtained between the observed probability of formation of H^3-*n*-pentane from H^3 recoils in *n*-pentane gas as a function of He^4 moderator concentration and the probability of collision of an H^3 atom with *n*-pentane before thermalization, calculated from simple collision theory (*67*).

With the establishment of the validity of the concept of hot atom reactions at relatively high kinetic energies it becomes of importance to study their systematic chemistry, to gain information as to their energy dependence and collision efficiencies, and to investigate the way in which energy is transferred and reaction is induced in the hot collision. After information of this type has been gained it should be possible to test the validity of the reaction models discussed in Section III,A.

In recent years the systematic chemistry of reaction of hot hydrogen atoms with organic molecules has begun to be investigated, using the $He^3(n,p)H^3$ or $Li^6(n,\alpha)H^3$ reactions with recoil energies of 2.730 and 0.192 Mev respectively (*128, 129, 247, 251, 302*).

A prominent scavenger-insensitive reaction in alkanes is substitution or displacement of a carbon-bonded hydrogen (*161–164, 301, 303*):

$$H^3 + RH \rightarrow RH^3 + H \tag{12}$$

$$CH_4 + H^3 \rightarrow CH_3H^3 + H \tag{13}$$

$$\begin{array}{l} CH_3CH_2CH_2CH_3 \rightarrow CH_3CH_2CH_2CH_2H^3 \\ \qquad\qquad\qquad\qquad\quad \searrow \\ \qquad\qquad\qquad\qquad\quad CH_3CH_2CHH^3CH_3 \end{array} \tag{14}$$

The high yield of the recoil tritium substitution reactions with molecules such as methane or cyclopropane (*77, 161, 163*), with which thermal hydrogen atoms react with low efficiency, confirms the hot or epithermal nature of the substitution reaction.

The moderator-sensitive part of the high organic yield of radio-iodine (*136, 169*), radiobromine (*104*) and radiochlorine (*51, 83*), observed when the halogens undergo radiative neutron capture in gaseous hydrocarbons as discussed earlier, shows that hot halogen atoms can initiate a direct displacement reaction of the type of Eq. (12).

Hot hydrogen abstraction is also commonly observed (*77, 129, 247, 303*):

$$H^3 + RH \rightarrow R + H^3H \tag{15}$$

e.g.,

$$\begin{array}{l} H^3 + CH_3CH_2CH_2CH_3 \rightarrow CH_3CH_2CH_2CH_2\cdot + HH^3 \\ \qquad\qquad\qquad\qquad\qquad\quad \searrow \\ \qquad\qquad\qquad\qquad\qquad\quad CH_3CH_2\underset{\cdot}{C}HCH_3 + HH^3 \end{array} \tag{16}$$

The abstraction reaction is also observed at thermal energies, although with a much lower collision yield (*16, 17*). It should be pointed out that observation of the HH^3 product is not in itself proof of abstraction, since this product might be eliminated from an excited molecule. On the other hand hydrogen loss would be random, so that the low yield of tritiated alkenes found in practice shows that H^3 elimination from an excited molecule is relatively unimportant.

A hot reaction with tritium may less frequently lead to replacement of an alkyl group to form a degraded alkane (*77, 78, 162, 303*):

$$\begin{array}{ll} H^3 + CH_3CH_2CH_2CH_3 \rightarrow & CH_3H^3 \\ & CH_3CH_2H^3 \\ & CH_3CH_2CH_2H^3 \end{array} \tag{17}$$

Fluorine, chlorine, bromine, and iodine in alkyl halides can be displaced by a hot hydrogen atom (*225*):

$$H^3 + CH_3X \rightarrow CH_3H^3 + X \qquad (18)$$

Halogens and nitro-groups can also be displaced by hot hydrogen reactions in aromatic systems (*247, 318*).

Relatively infrequently a hot tritium atom may displace two hydrogen atoms or one hydrogen atom and an alkyl group to form a radical (*129, 162, 303*), e.g.:

$$H^3 + CH_3CH_2CH_2CH_3 \rightarrow CH_3CH_2CH_2CHH^3\cdot \qquad (19)$$

The resulting radical may combine with iodine scavenger to yield an alkyl iodide, or it may break a C—C bond without rearrangement to give a smaller radical and an alkene:

$$CH_3CH_2CH_2CHH^3\cdot \rightarrow CH_3CH_2\cdot + CH_2{=}CHH^3 \qquad (20)$$

Only methyl and ethyl iodides have been found so direct combination with scavenger is only possible for methyl and ethyl radicals. Larger radicals always decompose by reaction (20) until methyl or ethyl radicals are formed.

In the case of recoil tritium reactions with alkenes it is found that most of the hot reactions are similar to those described for alkanes (*301, 302*). Oxygen can be used as a scavenger for thermal atoms and radicals. Some H^3-labeled alkenes of smaller molecular weight than the parent are formed in relatively large yields. It is proposed that in these instances a hot H^3 atom is added to a double bond, forming an excited radical, which will probably decompose to a smaller radical and an olefine by breaking a weak bond (*156, 186*):

$$\begin{array}{ccc}
\multicolumn{3}{c}{RCH_2CH{=}CHCH_2R' + H^3} \\
\swarrow & & \searrow \\
[RCH_2CHH^3{-}\dot{C}HCH_2R']_{hot} & & [RCH_2\dot{C}H{-}CHH^3CH_2R']_{hot} \\
\downarrow & & \downarrow \\
RCH_2CHH^3{-}CH{=}CH_2 + R'\cdot & & RCH_2CH{=}CHH^3 + \cdot CH_2R' \\
\text{or} & & \text{or} \\
RCH_2\cdot + CHH^3{=}CHCH_2R' & & R\cdot + CH_2{=}CHCHH^3CH_2R'
\end{array} \qquad (21)$$

Since the addition of a hydrogen atom to a double bond is exothermic one might expect the reaction to proceed with thermalized H^3 atoms. The yield of the product is not appreciably affected by small amounts of oxygen as radical scavenger, which suggests that the mechanism is not a thermal one. On the other hand, when helium is introduced as a moderator the yield of reaction products is greatly reduced (*301*).

It has also been shown that there is an increase in the yield of the major alkene fragments at low pressures (*166*), which indicates that one of the intermediates in the sequence of Eq. (21) is sensitive to collisional deactivation.

It should be borne in mind that yields of alkenes of lower molecular weight could in some cases be explained by direct displacement of alkyl groups. However, such a mechanism does not readily explain the large yields of $CH_2{=}CH_2$ and $CH_2{=}CHCH_3$ but small yield of $CH_3CH_2CH{=}CH_2$ from $CH_3CH_2CH_2CH{=}CH_2$, or the formation of $CH_3CH_2CH{=}CH_2$ from $CH_3CH_2CH_2CH{=}CHCH_3$.

There are considerable difficulties in extracting information from hot atom studies as to the energy dependence of collision efficiencies for high-energy interactions, or as to the modes of transfer of energy to the struck molecule. The Estrup-Wolfgang theory contains $p(E)$ in the definite integral, I, of Eq. (8). Nevertheless some information on collision efficiency energy dependence can be obtained by studying the relative energies at which various products can appear in a given system.

Tritium has been allowed to recoil in systems in which reactions with saturated or unsaturated positions are competitive. The specific activities of propane and transbutene, for example, are very similar after irradiation of a system containing a mixture of the two gases, indicating that a hot H^3 atom reacts with comparable efficiency at saturated and unsaturated positions (*162*), despite the fact that the relative rates of exchange with thermal deuterium atoms differ by a factor of more than 1000 (*298*). Varying the pressure of an inert gas moderator, such as helium, alters the energy distribution of the recoils in the range of their reaction-causing collisions with competing organic constituents. As the moderator concentration rises in the propane-acetylene system there is a linear rise in the specific activity ratio acetylene/propane (*247*). The reaction efficiency will start from zero at H^3 kinetic energies lower than the activation energy, then rise to a maximum, and again fall to zero at energies too high to allow stable bond formation during collision. The propane-acetylene results can be explained by assuming that the curve of reaction efficiency as a function of kinetic energy passes through its region of high efficiency at a lower energy value in the case of acetylene than in the case of propane.

When H^3 recoils through methane in the presence of I_2, CH_3H^3, and CH_2H^3I are formed as a result of the direct displacement and abstraction reactions:

$$CH_4 + H^3 \rightarrow CH_3H^3 + H \qquad (22)$$

$$CH_4 + H^3 \rightarrow CH_2H^3\cdot + H_2 \qquad (23)$$

When these reactions are allowed to occur in the presence of varying concentrations of helium or neon moderators and iodine scavenger, the curves of relative yields of CH_3H^3 and CH_2H^3I against mole fraction CH_4 are very similar, suggesting that the reactions of Eqs. (22) and (23) proceed with a very similar energy dependence of the reaction efficiency.

In general it is observed that displacement or abstraction reactions of the type of Eqs. (12) and (15) together account for about 90% of the hot H^3 reactions, while less than 10% involve displacement of an alkyl group as in Eq. (24) (*129, 303*). The probability of C—H bond rupture is thus about four times greater than that of the C—C rupture. This finding perhaps indicates that hot displacement reactions do not go via a common collision complex of sufficient lifetime to permit internal equilibration of energy. Magee and Hamill (*196*) have developed a theoretical treatment to account for photochemically hot reactions, i.e., 1–2 ev, which is based on the applicability of absolute reaction rate theory and the involved assumption of equilibration of energy between all degrees of freedom. Wolfgang *et al.* (*129*) consider that while this theory may be valid for the energy range for which it is intended, extension to the range which is of interest here is not valid since such an equilibrated complex should break a weak bond at least as often as a strong one. These authors point out that if HH^3 and $CH_2H^3\cdot$ were produced from methane by decomposition of a common activated complex with indistinguishable H^3 and CH_4 hydrogen atoms as follows:

$$\mathrm{H^3 + CH_4 \rightarrow [CH_4H^3]} \begin{array}{l} \nearrow \mathrm{CH_2H^3\cdot + H_2 \text{ or } CH_3\cdot + HH^3} \\ \searrow \mathrm{CH_3H^3 + H \text{ or } CH_4 + H^3} \end{array} \qquad (24)$$

then the ratio $HH^3/CH_2H^3\cdot$ would be expected on a statistical basis to be 2:3. In fact the highest value of the observed ratio is 9:1 (*77*).

Experiments on stereochemical effects in hot hydrogen displacement reactions throw further light on energy transfer in hot gas phase reactions. Recoil H^3 reacts with gaseous optically active *sec*-butyl alcohol to give 91% retention of configuration about the asymmetric carbon atom during displacement of the hydrogen bonded to it, or during displacement of the hydrogen in the methyl and ethyl groups (*128, 130*). Similar retention of configuration has been found in solid phase irradiations of optically active glucose (*146, 249*), alanine (*145, 250*) and maleic and fumaric acids (*247*), although the possibility of constraint to retain configuration by the surrounding lattice somewhat limits the usefulness of conclusions drawn from solid phase experiments.

The greater probability of C—H than C—C bond rupture, the retention of optical configuration, and the absence so far of evidence for equilibration of energy in the collision complex, have together suggested a rather simple mechanism for hot reactions with H atoms. It has been proposed (*128*), that the hot H^3 atom can approach the H atom, which will be removed, over a relatively wide range of directions. Approach along the C—H bond axis will not give displacement, since H^3H juxtaposition is hindered, although abstraction could occur in this situation. The picture is thus developed of approach of the hot H^3 atom within a cone of small angle leading to abstraction, while approach within a cone of wider angle leads to displacement.

A consequence suggested by this simple theory is that steric factors arising from molecular structure should influence the ratio of efficiencies for displacement and abstraction reactions. The abstraction/displacement ratio is found experimentally to be unity in the case of methane, having perhaps no obstruction for wide angle approach to any of the four hydrogens. As hydrogen atoms are replaced by the bulkier methyl or ethylene groups, the efficiency for the wide-angle displacement reaction should be reduced relative to that for the small angle abstraction, say by a factor $(1 - \Omega)$. Thus for an alkane containing n hydrogens, of which n_1 are primary, n_2 are secondary, and n_3 are tertiary, on the rather simple assumption that any attached group offers the same obstruction, we would expect:

$$\frac{\text{Abstraction yield}}{\text{Displacement yield}} = \frac{n}{n_1(1 - \Omega) + n_2(1 - \Omega)^2 + n_3(1 - \Omega)^3} \tag{25}$$

Using a value 0.45 for the obstruction parameter Ω, it has been found that a good correlation is obtained between the values of abstraction yield/displacement yield calculated from Eq. (25) and those obtained experimentally for a series of non-cyclic alkanes and cyclopentanes (*128*).

The dependence of abstraction/displacement ratios on steric obstruction of the displacement reactions has been disputed by Root and Rowland (*128*), who consider that abstraction is dependent on C—H bond strength and will be facilitated at a more weakly bonded secondary carbon. More work will be needed to resolve this point.

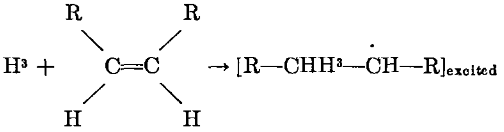
Considerations of steric hindrance would also suggest that displacement of an alkyl group as in Eq. (17) should be less frequent than displacement of an atom as in Eq. (12), and this is found to be the case (*128*). The probability of forming an alkane product RH^3 is found to increase with increase in the number of R groups in the molecule as expected, so that, for example, the relative yield of CH_3H^3 increases in the series cyclopentane < *n*-pentane < isopentane < neopentane (*128*). The reaction of recoil H^3 with neopentane yields eight times as much methane-H^3 as isobutane-H^3 (*128*), and this can be interpreted as showing that the H^3 preferentially reacts with the group which has the larger overall angle of approach, i.e., with the smaller of the two groups joined by the C—C bond.

Recoil H^3 reactions with toluene gas have been studied (*1*). The distribution of H^3 in the labeled toluene is CH_3, 22%; *ortho*-, 17%; *meta*-, 14%, and *para*-, 16%. There is thus a distinct preference for H^3 reaction with the methyl hydrogen, but a relatively minor orienting effect with regard to the ring positions.

Comparison of the activities in various products formed by H^3 recoils in gaseous alkenes with those obtained with alkanes lends further support to the "cone-of-approach" interpretation of hot hydrogen reactions outlined above. Abstraction and displacement reactions will occur at C—H sites in alkenes in the same way as in alkanes, but in addition reaction at the double bond will yield decomposition products by the mechanism of Eq. (21), thus reducing the yields of HH^3 and H^3-parent type molecules. One would thus expect a rise in the relative yield of HH^3 with increase in number of carbon atoms in a mono-alkene, and that this yield should always be smaller than for the corresponding alkane. This is found to be the case (*302*).

In considering the transfer of energy to a struck molecule in a hot reaction it must be remembered that unless the departing group takes off all excess energy the radioactive daughter molecule will not be in thermal equilibrium with its environment. Excess energy may be removed by collision, or may lead to decomposition or intramolecular rearrangement of the hot reaction product. In cases in which collision deactivation competes with decomposition or rearrangement, the distribution of reaction products will be sensitive to gas pressure or presence of an inert moderator. When H^3 recoils in cyclopropane with NO scavenger, for example, a displacement reaction leads to formation of a vibrationally excited H^3-cyclopropane molecule. This molecule can isomerize to propylene. The propylene yield decreases with increase in the pressure of cyclopropane (*163*, *247*). Similar reactions have been observed with *cis*- and *trans*-1,2-dimethyl-cyclopropane (*247*).

The pressure-sensitivity of the yield of the major fragments from the reaction of hot H^3 with alkenes (*166*) has already been mentioned in this section. It has also been shown (*162*, *247*) that recoil H^3 reacts with olefins to yield a radical:



$$H^3 + \begin{matrix} R & & R \\ & \diagdown\quad\diagup & \\ & C{=}C & \\ & \diagup\quad\diagdown & \\ H & & H \end{matrix} \rightarrow [R{-}CHH^3{-}\dot{C}H{-}R]_{\text{excited}} \qquad (26)$$

A pressure-dependent competition is found to exist between decomposition of the radical:

$$[R{-}CHH^3{-}\dot{C}H{-}R]_{\text{excited}} \rightarrow R + CHH^3{=}CHR \qquad (27)$$

and collisional de-excitation to a thermal radical which reacts to give a saturated molecule. Thus the yield of labeled propylene from *trans*-butene-2 and *cis*-butene-2 via the reaction of Eq. (34) is higher at lower pressures.

The amount of excess energy transferred to the hot reaction product must often be small, since the yield of radioactive products requiring multiple bond rupture is frequently low. Only traces of acetylene, for example, are formed from hot H^3 reactions with alkanes, while the yield of methyl acetylene and allene by reaction with alkenes is less than 1% *(128, 165)*. The small amount of excess energy in the hot reaction product can sometimes effect an intramolecular rearrangement without decomposition. Thus it is found *(128)* that in 30% of hydrogen displacements at the sp^2 carbon atom in *cis*- and *trans*-dichloroethylenes the initial configuration is lost by an intramolecular process which has an energy of activation of about 2 ev. The fact that such a low energy intramolecular process occurs in a minority of events, together with the infrequency of multiple bond rupture, suggests that the amount of excess energy deposited in the hot reaction product is often very small, and it may require a relatively low energy process of isomerization e.g., rotation about a double bond to reveal it. This suggestion is supported by the finding that in the stable alkanes, where the only collisional process which could dissipate the excess energy is decomposition into radicals, the yield of such radicals is found to be only $\sim$5%. In addition part of the observed radical yield could have been given directly by a process of the type shown in Eq. (19). In the case of the isomerization of cyclopropane to yield propylene, discussed in the previous paragraph, the energy of excitation of the H^3-cyclopropane daughter must have been about 4 ev, by comparison with the known energy of 3 ev for this isomerization when accomplished thermally.

The picture of hot hydrogen reactions in the gas phase outlined in previous paragraphs is thus one of a predominance of hydrogen displacement and abstraction reactions, the relative frequency of these depending on the angle of approach of the incoming H^3 to the struck hydrogen atom. In the case of the direct displacement reaction it is interesting to enquire if this occurs as a result of a single billiard-ball collision of the type outlined in Section III,A. The evidence of alkyl group replacement and intramolecular rearrangement given above already shows that some energy is transferred to the rest of the struck molecule. Direct evidence has been obtained of the inadequacy of the simple billiard-ball model from experiments with H^3 recoils in CH_4 and CD_4 *(66)*. On the basis of classical mechanical collision theory of the type underlying the Wolfgang-Estrup kinetics, the billiard-ball model predicts an isotope effect of 3.06 for the ratio I_{CD_4}/I_{CH_4}, where I is defined by Eq. (10). This can be seen intuitively from the fact that H^3 will be more effectively stopped in a head-on collision with D than with H. In fact no isotope effect greater than 20% is found. Thus the simple billiard-ball mechanism is not probable for gas phase H^3 reactions. Energy must be coupled into the struck molecule, and this in turn necessitates that the bulk of the displacement reactions must occur in the "strong-coupling" epithermal region with H^3 energies $<\sim$10–20 ev.

Recent experiments throw light on the mechanism of displacement of heavy atoms and groups by H^3 recoils (*225*). In the series CH_3F, CH_2F_2, CHF_3, and CF_4, with scavenger added to suppress thermal reactions, there is a decrease of probability of displacement of F by H^3 from a value of 5.3% per C—F bond in CH_3F to 0.1% per bond in CF_4. On the other hand there is a much smaller decline of H replacement by H^3. A parallel result is obtained for the chloro- and bromo-methanes. The small decline in H replacement can be explained as an effect of steric hindrance on the wide-angle approach of H^3 to the struck atom, as outlined in previous paragraphs. In the case of an F atom struck by H^3 the greater mass of the fluorine may cause it to move away from its bond more slowly than a struck H atom, so that the incident H^3 may take more time to occupy its position. Thus the H^3 tends to be further from the position required for sp^3 binding and may more readily escape or be scavenged by the displaced fluorine. On the other hand rotation of the struck molecule may bring the H^3 atom into the correct alignment for tetrahedral binding. The authors of the work consider that the heavier the substituents on the struck molecule, the less likely is sufficiently rapid rotation to be accomplished and the lower will be the H^3 retention. No such restriction applies in the case of H^3-H replacement. This model for the first time suggests a rotational component of importance in hot reactions. The writer feels, however, that the mechanism may need to be found in terms of competitive reactions of the dislodged F atom and the carbon-containing radical with the H^3 atom, without evoking a rotational mechanism. Available thermochemical data indicate a lower energy of activation for H^3 reaction with $CH_3\cdot$ than with $CF_3\cdot$.

Further light on high-energy gas phase reactions has come in recent years using radioactive carbon recoils. Recoil C^{14} atoms from the reaction $N^{14}(n,p)C^{14}$ have an initial kinetic energy of 45,000 ev. The cross-section for activation of N^{14} with pile neutrons is small and the C^{14} half-life is long, so that gas phase studies require high-sensitivity C^{14} assay procedures, and analytical techniques for separation of trace amounts of labeled products (*82*, *334*, *335*, *338*), as well as irradiation times of a few days at thermal neutron fluxes of $\sim 10^{13}$ n/cm^2/sec. The relatively high gamma doses which accompany such irradiations introduce the undesirable complication of radiation-promoted reactions (see Section III,C). To overcome this limitation use has recently been made of the 20.5 minute C^{11} produced by a neutron transfer reaction between a beam of 120 Mev C^{12} ions and a platinum foil (*184a,b*).

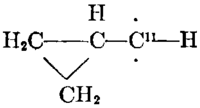
When hot C^{11} atoms are allowed to pass into gaseous O_2, NO, NO_2, N_2O, Co, CO_2, and SO_2, the main product in all cases is $C^{11}O$ (*184a,b*). CO_2

formation is low in all systems except the oxides of nitrogen, where it can rise to as much as 43% of the total volatile activity. The reaction of C with O_2 is strongly exoergic so that in absence of a third body $C^{11}O_2$ will decompose. This limitation does not apply in the case of reactions with NO_2 and CO_2 to form $C^{11}O_2$, and it is suggested (*184a,b*) that the high yield of the radioactive monoxide in these cases is due to the greater ease with which the incident C^{11} atom can displace a terminal atom in the complex with molecules such as O═C═O, O═N═O, or O═S═O. The high yield of $C^{11}O_2$ in the case of N_2O must result from $C^{11} + N_2O \rightarrow C^{11}O + N_2$ as the highly exoergic primary reaction. By analogy with other systems, such as H reaction with O_3, in which a nonequilibrated energy distribution in the products yields a high proportion of energy in the product containing the new bond (*182*), it is suggested that the highly excited $C^{11}O$ reacts further by $C^{11}O + N_2O \rightarrow C^{11}O_2 + N_2$.

When C^{11} recoil atoms react with H_2, $C^{11}O$, and $C^{11}H_4$ are formed in roughly equal yields (*184a,b*). The monoxide arises from oxygen impurity in the gas or on the vessel walls. Such a high sensitivity to oxygen suggests a low reactivity of C atoms with H_2. C^{14} recoils give a high yield of CH_4 in gaseous ammonia after a pile irradiation involving $\sim 2.4 \times 10^8$ rads gamma dose (*329, 338*). C^{11} atoms in an X-ray field of low intensity do not form methane in gaseous ammonia, but when some radiolysis is allowed to occur $C^{11}H_4$ is found as the major product (*184a,b*), so that we are presumably not observing a high-energy methane synthesis.

Recoil C^{11} has been allowed to react with gaseous hydrocarbons (*184a,b*). The chief results can be summarized as follows.

The main product in all systems is $C^{11}H{\equiv}CH$. Since this product occurs after recoil in methane it can result from C^{11} reaction with C—H bonds ("C—H bond insertion"). In the case of cyclopropane the yield of $C^{11}H{\equiv}CH$ is about twice as high as in other systems. C—H bond insertion here would yield:



which can decompose into ethylene and acetylene simply by electronic rearrangement without group migration. This may favor the observed high acetylene yield by comparison with other systems in which acetylene formation cannot occur at all carbon atoms by simple electronic rearrangement. In the addition of C^{11} to propane sufficient energy is released to allow rearrangement to $CH{\equiv}CH$ in 25–30% yield, $CH_2{=}CH_2$ in 12–20% yield, and unsaturated C_3 fragments. Less drastic rearrangement can yield

$CH_2{=}C(CH_3)CH_3$ in 1.5–2.4% yield and $CH_3CH_2CH{=}CH_2$ in 2.5–3.0% yield (*185*).

C^{11} recoils can also react with C=C bonds. Yields of stable carbon addition products are higher in the case of $CH_3CH{=}CH_2$ irradiations than in the case of $CH_3CH_2CH_3$. It is suggested that the first step is direct C^{11} addition to the double bond, followed by electronic rearrangement, breaking of a C—C bond and H atom migration in the excited intermediate (*184a,b*).

Significant amounts of C^{11}-*n*-butane and isobutane are formed when C^{11} recoils in propane, suggesting that the methylene radical may be involved, but the yields show this to be less frequent than the direct insertion reaction.

No evidence has as yet been obtained in gas phase studies of a C—C bond insertion reaction. If this occurs at all it is much less probable than the reactions outlined above.

The chemistry of N^{13} recoils from the $C^{12}(d,n)N^{13}$ reaction in various gases has been studied in recent work (*155*, *260*). Cyanides are mainly formed in the alkyl halides. HCN is the chief product, although halocyanides appear in greater yield as the amount of halogen in the target gas increases. No ammonia is found, suggesting that an abstraction reaction may not be occurring. In work with highly energetic deuterons it is difficult to avoid radiation effects since a fairly dense column of ions and radicals will be formed along the deuteron track. In the case of the reaction of N^{13} recoils with methanol vapor, the distribution of reaction products was not significantly influenced by addition of Br_2 scavenger so that some truly hot reactions may be involved.

2. Hot Reactions in the Liquid Phase

Although many aspects of high-energy reactions consequent on nuclear activation have been clarified by gas phase studies of the type described in the previous section, the bulk of the earlier work from which the concept of hot reactions emerged was done in liquid and solid organic halides, utilizing the (n,γ) reaction. The organic halides were convenient because the relatively high neutron capture cross-sections and the short half-lives of the activated halogen atoms allowed work with low intensity neutron sources. The relatively well explored photochemistry of these compounds permitted comparison with reaction mechanisms activated by light absorption. Thermally activated halogen-halide exchange reactions were found to proceed to a negligible extent in systems selected for study, although this possibility has to be borne in mind (*190*).

Three complications presented themselves in the course of this work. In the first place minute amounts of impurities capable of reacting with thermalized halogen atoms could obscure the effects of reactions specifically activated by energy derived from the nuclear process, and rigorous procedures had to be adopted for purifying target materials (e.g., *202, 319, 323*). Preparative gas chromatography on a scale capable of handling the required amounts of targets should make an important contribution here (*126*). A second difficulty was that of calculating the exact spectrum of recoil energies from the (n,γ) reactions, although as discussed in Section I,A,*1* the spectrum from the $Cl^{35}(n,\gamma)Cl^{36}$ reaction has recently been evaluated with reasonable accuracy, and procedures are available for dealing with the other reactions when gamma cascade schemes become better known. This difficulty has not seriously impeded work in the field, one reason being that many product distributions seem to be independent of the initial energy of the recoil, as described later. The third difficulty of work with organic halides has been the large number of reactions involved and the large variety of products formed (e.g., *54, 286, 323*). This has undoubtedly greatly complicated the initial chemical interpretation of the reaction mechanisms, and has necessitated development of techniques for the separation of trace amounts of radioactive products for which often no carrier could be added. The rapid advances recently made in this field have been greatly facilitated by the application of gas chromatography, coupled with high sensitivity radiometric assay of the separated products (*82, 84, 126, 131, 144, 274, 334, 335, 338*).

Evidence was obtained in earlier work which supported the view that the billiard-ball mechanism of Libby, outlined in Section III,A, could account for at least some of the organic retention in the liquid phase. As predicted by this model, in organic halides the greater part of the organic retention frequently occurred in compounds of the parent type (*34, 91, 93, 171, 172, 323*), although this was not found to be the case with the polyvalent atoms of phosphorus (*36, 37, 272*), arsenic (*37, 191, 273*), and antimony (*115*). The prediction that solid compounds should show a greater retention than the same compounds in liquid state, due to a more pronounced caging effect round the collision site was fulfilled in the case of several organic halides (*51, 91, 93, 99, 167, 240*), although this was not found to be the case in C_2H_5I, i-C_4H_9I, or s-C_4H_9I (*167*). The retention during irradiation of a solid phase was found to be dependent on the crystalline structure of the phase in the case of n-C_4H_9Br (*248*).

The effect of dilution with an "inert" solvent in lowering the retention in organic halides (*171, 172, 200, 305*), or in organic arsenic compounds when radical scavengers are used to suppress thermal reactions (*37, 272, 273*), can readily be interpreted as a result of moderation of the recoil to energies below those effective for the billiard-ball mechanism (*172*). It should be pointed out, however, that retention of P^{32} in butyl esters of phosphoric acid in the presence of oxygen as radical scavenger is increased on dilution with *n*-heptane or benzene (*272*), although in this case the solvent may not be inert. The noninert nature of the diluent can lead to increase in organic retention in the case of organic halides diluted with hydrocarbons (*100*, *200*).

Evidence soon accumulated to show that the elastic-collision model could not account for all high-energy organic retention in the liquid phase. It was found that solutions of elementary halogens in hydrocarbons could yield organically retained radioactivity on neutron irradiation (*19*, *51*, *93*, *99*, *100*, *136*, *178*, *200*, *239*, *262*, *321*). Similarly, phenyl arsenic compounds were found to be formed by neutron irradiation of arsenic trichloride in benzene (*37*, *58*, *273*). Under these conditions retention-causing collisions of the billiard-ball kind envisaged by Libby are excluded. In addition many compounds other than the parent type were often found in the organic radioactive fraction after neutron irradiation of the organic halides (*34*, *93*, *98*, *127*, *132*, *203*, *286*, *323*), contrary to the expectations of the original billiard-ball mechanism.

By adding traces of elementary halogen as inorganic and organic radical scavengers to organic halides before neutron irradiation, it was found that at least two kinds of retention-causing mechanism were operative in the liquid phase. The first mechanism presumably involves diffusion of radicals over a sufficient distance to give a high probability of their interception by traces of elementary halogen, and was revealed by a sharp drop in the curve of organic retention versus mole fraction of scavenger at low concentrations of the latter. The second mechanism presumably involves hot localized reactions, and is operative in the region of the curve which was insensitive to scavenger concentration (*100*, *137*, *167*, *203*, *205*, *319*). A typical curve of organic retention versus scavenger concentration is shown in Fig. 8. It is possible that the effect of aniline in depressing the organic retention, discovered by Lu and Sugden (*175*), may be due to a similar radical scavenging action of amines, since the curves of retention as a function of scavenger concentration, and the distribution of radioactive products are similar for aniline, butylamine and bromine additives (*34*), although other explanations can be advanced for this effect (*132*, *172*, *286*). Willard and Goldhaber (*100*) have discussed nine possible elementary reactions involving radiobromine from the point of view of their classification as hot or thermal on the basis of the scavenger method.

The finding that a multiplicity of products can be obtained both in gas and liquid phase irradiations in the presence of halogen scavengers (*323*) shows that a number of reactions must be of the bimolecular displacement type, rather than reactions of the radioactive atom with radicals after diffusion. In the liquid phase conditions are complicated by comparison with gas irradiations. The finding that in the liquid phase radical scavengers depress the yield of radioactive organic products, together with the formation of radioactive organic species by halogen recoils in pure hydrocarbons, indicates that many inelastic collisions occur during recoils in liquids, leading to fragmentation of molecules, and that the radioactive atom is combining with these fragments. Such findings constituted the earlier experimental basis of the random fragmentation theory of Willard, outlined in Section III,A.

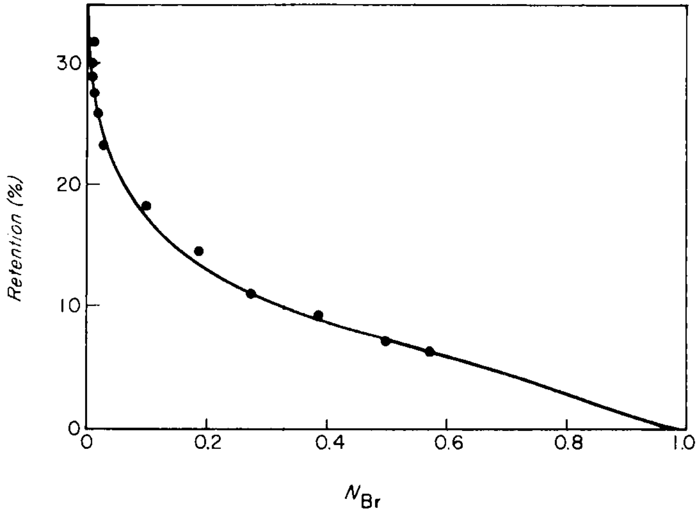


FIG. 8. Organic retention of Br^{80m} in neutron irradiated ethyl bromide as a function of the molar fraction, N_{Br}, of bromine (*202*).

It has been of considerable interest to use the scavenger technique to obtain data on the systematic chemistry of the scavenger-insensitive hot reactions, the effects of environmental conditions on their yields, and their dependence on the kinetic energy of the recoiling species.

The effect of Br_2 scavenger on the yield of eleven organic-Br^{82} products formed by the $Br^{81}(n,\gamma)Br^{82}$ reaction in *n*-propyl bromide and isopropyl bromide has been determined (*54*). Three classes of products were observed. Products such as 1,1,2-tribromoethane and higher boiling point fractions had their yield increased threefold by the bromine scavenger at 5 mole % concentration. It is suggested that this type of product is formed when a bromine molecule is present at the site where the Br^{82} enters into combination by a hot process, so that the scavenger molecule is involved in synthesis of the new compound. An alternative explanation might be the formation of a Br^{82}-olefin during a hot collision, and subsequent addition of Br_2 to this molecule. A second class of products is that for which a relatively small depression of yield is caused by the addition of scavenger. This group includes 1,3-dibromopropane, 1,2-dibromopropane, *n*-hexyl bromide' ethylene bromide (from *n*-propyl bromide) and methylene bromide (from isopropyl bromide). The third group includes those compounds for which the yield is depressed by 35% or more by addition of the scavenger, and in which hot and thermal reactions are thus involved to roughly the same extent, viz., *n*-propyl bromide, isopropyl bromide, ethyl bromide, methyl bromide, and ethylene bromide (from isopropyl bromide). It seems that in this system compounds which may result from reaction of a thermalized Br^{82} atom with a radical formed by the breaking of a C—Br or a C—C bond are more susceptible to scavenger action than those which involve the breaking of C—H bonds. Reactions involving C—H bond rupture thus tend to be either a one-step displacement reaction of the type of Eq. (12), in which a bromine replaces a hydrogen atom, or a combination with a radical formed in a collision by H removal before that radical has had a chance to move more than a very few molecular diameters.

In the case of neutron irradiation of CH_2Br_2 and $CHBr_3$ (*34*) yields of CH_2BrBr^{80} and $CHBr_2Br^{80}$ from Br—Br displacement or from radical formation by C—Br bond rupture were found to be depressed by scavenger by 21% and 26%, respectively. On the other hand yields of higher bromoderivatives were depressed by scavenger as follows: in CH_2Br_2 target, $CHBr_2Br^{80}$ depressed by 59%, and CBr_3Br^{80} + higher boiling point fractions depressed by 55%; in $CHBr_3$ target, CBr_3Br^{80} + higher b.p. fractions depressed by 51%. Thus only about half the processes involving radical formation by C—H bond rupture or hydrogen substitution are hot in this system. Later work on the system (*126*) has yielded similar values for the scavenger-sensitive fraction of the yields of parent-type molecules, and has shown the extensive participation of hot processes in reactions yielding products more highly brominated than the parent molecule. Work on this same system and other halo-methanes has revealed some discrepancies, however, the following values being obtained for the participation of scavenger-sensitive processes in reactions leading to formation of the parent molecule (*220*): Br^{80m} and Br^{82} in CH_2Br_2, 59%; Br^{80m} and Br^{82} in $CHBr_3$, 51%; Br^{80m} in CCl_3Br, 63%; Br^{82} in CCl_3Br, 65%; Br^{80m} in CCl_2Br_2, 41%; Br^{82} in CCl_2Br_2, 50%. The basis of the disagreement on the relative role of hot processes in forming parent CH_2Br_2 and $CHBr_3$ is not clear, but may be due to differences in purification procedures.

The yield of CCl_3Br^{80} from neutron capture by elementary bromine in CCl_4 decreases at first rapidly and then more slowly with increase in bromine concentration (*137*). The yield of CCl_2BrBr^{80} goes through a maximum and then declines, while the yield of higher b.p. material goes through a minimum followed by a maximum. It is found that the mono-bromo parent is being formed by processes which are ~50% hot and ~50%

involving thermalized Br^{80} atoms. The formation of the dibromo-derivative probably proceeds via production of a $CCl_2Br^{80}\cdot$ radical in a high-energy collision. At high Br_2 concentrations CCl_2BrBr^{80} formation will ensue, but at low Br_2 concentrations $C_2Cl_5Br^{80}$ will be formed, accounting for the peak in the higher b.p. yield.

In the case of a liquid CH_3I target the addition of iodine scavenger depressed the yield of CH_3I^{128} from the (n,γ) reaction by $\sim$43%, whereas the yield of CH_2I_2 was not significantly influenced and a small increase appeared in the yield of higher b.p. fractions (*167*).

Analysis of curves of organic retention versus scavenger concentration for the organic halides suggests that in addition to scavenger-sensitive thermal reactions and scavenger-insensitive hot reactions there is a group of reactions which is slowly suppressed by high bromine concentrations (*126*). This group has been called "hot-spot diffusive" to illustrate the concept that a hot atom may yield the last portions of its energy in a "hot spot" in a liquid, similar to terminal hot spots in recoil tracks in solids (*124*, *339*), and then may combine in this region with local decomposition products. High bromine concentrations are necessary before a reasonable probability exists of a scavenger molecule being found in such a hot spot. An example of such a reaction is that leading to the formation of bromoethane by combination of two one-carbon fragments formed in the hot spot, requiring $\sim$50% mole fraction Br_2 to depress its yield by a significant amount (*126*). A second example is the formation of parent type molecules from neutron-irradiated CH_2Br_2 or $CHBr_3$, quoted earlier. Analysis of the curves of organic retention versus scavenger concentration suggests that CH_2BrBr^{80} molecules are formed in neutron-irradiated CH_2Br_2 by processes which are 21% hot, 47% hot-spot diffusive, and 32% thermal. The analogous figures for $CHBr_3$ are 32%, 45%, and 23% respectively (*126*). On the other hand preliminary experiments on other bromo-alkanes suggest that classification into hot, hot spot-diffusive, and thermal processes may not always be so clear cut (*126*).

The probability of formation of radioactive organic products by high-energy processes should be proportional to the probability of a hot atom encountering a molecule capable of undergoing a retention-causing reaction during the high-energy part of its recoil, i.e., the high-energy retention, R_E, should be proportional to $1 - N_s$, where N_s is the mole fraction of scavenger. Such linear relationships have been found for bromine (*202*) and iodine (*167*) at scavenger concentrations above those necessary to suppress hot reactions. Fig. 8 shows a typical example. Extrapolation of the high energy region of the curve to zero scavenger concentration yields the fraction of retention-causing collisions occurring by means of a hot process (*100*, *252*). For a given reaction product the ratio of R_E at

$N_s = 0$ to R_E at $N_s = 0.27$ is $[1/(1 - 0.27)] = 1.37$. Products which show a greater ratio than this are presumably being formed in part by thermal, diffusive processes. Milman and Shaw (*202*) have used this analysis to examine the division of the products found in neutron-irradiated C_2H_5Br into those formed by hot and by diffusive processes. The percentage participations of hot processes in the reactions leading to formation of a given product were: $C_2H_5Br^{80}$ (parent), 26%; CH_2BrBr^{80}, 79%; $CH_3CHBrBr^{80}$, 66%; $CH_2BrCH_2Br^{80}$, 92%; CBr_2CBrBr^{80} (residue), 100%. When it is remembered that ~78% of the organic retention is in the parent molecule it is clear that the majority of diffusive reactions yield the parent molecule.

If billiard-ball collisions were predominant in the high-energy processes, then one might expect an increased participation of R_E in the over-all retention with increase in the number of bromine atoms per molecule. Milman and Shaw (*203*) have used the extrapolation method of the previous paragraph to obtain the following values of R_E/R_{total} in the stated target molecules: C_2H_5Br, 14%; CH_2BrCH_2Br, 17%; CH_3CHBr_2, 19%; $CH_2BrCHBr_2$, 17%; $CHBr_2CHBr_2$, 18%. These findings suggest that the high-energy interactions in this series are not a simple elastic-collision replacement process of the billiard-ball type. In a bromine-rich medium the recoil will be much more rapidly thermalized because Br—Br collisions are more effective for energy transfer than Br—C or Br—H collisions (*172*). Since the energy transfer process is thus more localized in the case of bromine-rich molecules, a thermalized recoil will find itself in a region of higher local radical concentration than in the case of mono-bromo-derivatives. One might therefore conclude that the chance of recoil-radical combination prior to the scavenger-sensitive diffusive process should be greater, i.e., R_E/R_{total} should be higher in the bromine-rich molecules. However, in the case of the bromine-rich molecule there is more chance of the radical which combines with the recoil being a Br atom, leading to inorganic retention. This local generation of atomic scavenger may account for the saturation effect observed for R_E as the number of bromine atoms per molecule is increased.

In contrast to the saturation effect of the previous paragraph, Nesmeyanov and co-workers (*220*) have found an increase of 6–8% in the hot process yield of the radioactive parent molecule per added Br atom in the series CCl_3Br, CCl_2Br_2, CH_2Br_2, and $CHBr_3$. These authors have concluded that the elastic collision model gives an adequate account of at least part of the hot processes leading to formation of the parent-type molecule. In the case of CH_3Br, CH_2Br_2, and $CHBr_3$ the amount of parent molecule formed by hot reactions was approximately in the ratio 1:2:3, which suggests that the chance of forming radioactive parent molecules by a hot process is directly proportional to the number of Br atoms available for replacement by collision with an energetic Br atom (*127*). Evidence for an increase in retention due to increased efficiency of moderation in a small volume has come from experiments in which the yields of bromoethanes from CH_3Br, CH_2Br_2, and $CHBr_3$ were 3.1, 6.2, and 10.3%, respectively (*125*). The higher concentration of reactive fragments thus induced would be expected to cause a higher proportion of bromoethanes, since the formation of a bromoethane requires a collision between two one-carbon fragments.

It would be of considerable interest to extract from the data any information as to whether the high-energy retention in organic halides is produced by a process which can be treated as essentially an atom-atom collision, or whether the process involves the struck molecule as a whole. Evidence for involvement of the whole molecule in gas phase experiments with H^3 has already been discussed in Section III,B,*1*. The difficulty of theoretical treatment of polyatomic molecules has been indicated in Section III,A.

Nesmeyanov and co-workers have proposed that the probability of molecular dissociation and thus of high-energy retention might be related simply to the maximum fraction of energy which can be transferred as internal energy to a struck molecule of mass M by a recoil of mass m. This fraction is $M/(m + M)$ of the energy transferred in the collision. When the retention in monosubstituted products is plotted against $M/(m + M)$ a straight line is obtained for a number of aliphatic bromides and chlorobromides (*218, 220, 222*). This suggests that the probability of a hydrogen displacement by a bromine atom may be proportional to the excitation energy of the struck molecule. The lack of isotope effect in H^3 displacement reactions in CH_4 or CD_4 gas, indicating coupling of energy into the whole molecule as mentioned in Section III,B,*1* seems to bear on this same point. In addition it has been found that increased Br^{80} retention accompanies increased molecular weight in the series from ethyl to *n*-amyl bromide (*286*).

Some evidence has been obtained that hot reactions, revealed by the scavenger technique, can be subject to specific chemical influences within the molecule. The ratio of *ortho-* to *meta-* to *para*-isomers of bromofluorobenzene formed as a result of the (n,γ) process in 3 mole % solutions of Br_2 in C_6H_5F is about 3:2:3, instead of the 2:2:1 ratio expected if hydrogen displacement occurred on a purely statistical basis (*323*). It is interesting to compare this finding with the relatively simple picture advanced in Section III,B,*1* to account for hot reaction mechanisms in H^3 recoil studies, in which steric availability of carbon-bound hydrogen atoms mainly seems to govern the probability of their displacement. Irradiation of C_6H_5I seems to yield only the $C_6H_5I^{128}$ product; C_6H_5Br yields $C_6H_5Br^{82}$ and

$C_6H_4BrBr^{82}$ isomers; while C_6H_5Cl yields $C_6H_5Cl^{38}$, $C_6H_4ClCl^{38}$ isomers and ~10% aliphatic chlorides, so that the number of detectable species increases from iodo- to bromo- to chloro-benzene (*323*). More importantly, perhaps, the aromatic ring seems relatively resistant to rupture in hot collisions, and this recalls the finding in H^3 recoil studies in gaseous alkanes, mentioned in Section III,B,*1*, that the energy coupled into the molecule is generally insufficient to cause extensive C—C bond rupture. When the $Br^{81}(n,\gamma)Br^{82}$ reaction takes place in 3 mole % Br_2 in C_6H_5Br, C_6H_5Cl, and C_6H_5F the yields of $C_6H_5Br^{82}$ are 22, 16, and 3%, respectively, indicating that displacement of the carbon-bound halogen atom from the aromatic ring is progressively more difficult in going from bromine to fluorine. This is perhaps one more piece of evidence to be added to that given earlier in this section for the idea that increased efficiency of energy transfer in elastic collisions may be related to the probability of displacement reactions, since the energy transfer efficiency declines in the series Br—Br, Br—Cl, Br—F collisions.

Willard (*319*) has pointed out that in addition to chemical properties the physical features of the medium may play an important part in deciding the course of high-energy interactions in the liquid phase. In a liquid the molecule struck by a recoil is backed by a close-packed and sometimes intertwined wall of other molecules, so that energy may be dissipated by breaking bonds in a rather indiscriminate fashion. Little work has been done so far to investigate this aspect of high-energy reactions, although it would seem that a useful approach might be a systematic study of the relative role of hot processes in the formation of separated products as a function of inert diluent concentration, or as a function of the viscosity and molecular complexity of the irradiated target.

It has been suggested (*99*) that an increased caging effect might result from a decrease in free space between the molecules (i.e., an increase in density), or from a change in molecular aggregation, or from a combination of these. In the case of neutron-irradiated CCl_3Br the progressive drop in retention, broken sharply at the melting point, as temperature is increased, has been explained as due to the decrease in density and diminished caging effect (*99*). The increase in organic retention due to hot processes in (n,γ) activation of iodine or bromine in hydrocarbons increases with increase in chain length from *n*-pentane to *n*-octane or *n*-decane (*2*, *100*). This may be due to increased molecular intertwining in the cage walls. A similar explanation might account for the finding that the organic retention after neutron irradiation increases with chain length in the homologous series of alkyl bromides from methyl to amyl and possibly hexyl bromide (*143*, *286*). It should be pointed out, however, that there is no increase in retention in the series CH_3I, C_2H_5I, n-C_3H_7I, and n-C_4H_9I when irradiated in the liquid or solid phase (*167*). In addition there is no clear evidence that the increased retention in the homologous series from ethyl to *n*-amyl bromide is due to increase in the proportion of smaller molecular size products (*286*), which might have been expected to be the case if increased intertwining of molecules had resulted in more extensive molecular fragmentation in a high-energy collision. The increased retention seems to be mainly in molecules of the parent type.

An important approach to the study of hot reactions in the liquid phase is the examination of their dependence on the kinetic energy of the recoiling fragment. For work with halogen-containing compounds the effects of the isomeric transition $Br^{80m} \rightarrow Br^{80} + h\nu$ in molecules labeled with Br^{80m} can be compared with the effects of the $Br^{79}(n,\gamma)Br^{80}$, $Br^{79}(n,\gamma)Br^{80m}$ and $Br^{81}(n,\gamma)Br^{82}$ reactions. As discussed in Section II,E, the isomeric transition yields a recoil energy which is much less than that needed to break chemical bonds, but a highly charged species may result from internal conversion. In the case of the (n,γ) reaction there is a considerable kinetic energy of recoil, and charge may also be acquired as a result of internal conversion of some of the weaker quanta in the gamma cascade (*314*). Comparison of the chemical consequences of the two types of nuclear process may thus throw light on the relative effects of kinetic energy and charge neutralization in the observed hot reactions. This type of comparison has been used to study the role of kinetic energy versus Auger charging in the decomposition of bromate ions in solution and in the solid state (*32*, *33*, *35*, *293*). Comparison of the consequences of the three (n,γ) reactions for bromine given above might also be expected to illuminate the role of initial recoil energy in hot reactions. In addition, by varying the energy of the neutrons captured in the (n,γ) process it is possible to vary the recoil energy.

In the case of iodine-containing compounds comparison has been made of the effects of the $I^{127}(n,\gamma)I^{128}$, $I^{127}(\gamma,n)I^{126}$, $I^{127}(d,p)I^{128}$ and $I^{127}(n,2n)I^{126}$ processes. The (γ,n) reaction yields recoils with a maximum kinetic energy for single quantum emission of 182 ev, although mutual momentum cancellation will reduce the effective recoil energy in most of the events, as discussed in Section I,A,*1*. The recoil energies from the $(n,2n)$, (d,p), and (γ,n) processes are of the order of 100,000 ev.

With elementary iodine present as scavenger the organic retentions in CH_3I and C_2H_5I subjected to (d,p), $(n,2n)$, (γ,n) and (n,γ) reactions were found to be the same (*261*). It is also interesting that the yields were similar from the hot plus diffusive reactions in the nonscavenged targets. Comparison of the retentions for the $(n,2n)$ and (n,γ) reactions in air-saturated C_2H_5I, *n*-C_3H_7I, *iso*-C_3H_7I, *n*-C_4H_9I and *sec*-C_4H_9I showed very similar values in both solid and liquid targets (*177*). Furthermore, the distributions of activity in the various products formed from the (n,γ) and $(n,2n)$ reactions in solid or liquid C_2H_5I were similar. The implication from these studies is that the retention-causing reactions are very little influenced by the magnitude of the kinetic energy supplied to the recoil by the nuclear event. This would be consistent with the view that the radioatom does not have a significant probability of combining with species formed by molecular fragmentation at the commencement of its track, but that the retention-causing hot reactions (and of course the diffusive reactions) occur predominantly towards the end of the track, when the recoil has significantly cooled. The situation in this case would resemble that discussed for chemical reactions undergone by recoils in solids, in which the initial recoil energy may not be important, and the decisive region for chemical reaction may be a terminal "hot zone" in which $\sim$300 ev of energy are dissipated in a small volume, causing melting, chemical decomposition and vacancy production in the lattice around the recoiling species (*123, 124, 339*).

In contrast to the above findings it has been observed that when equimolar mixtures of CH_3I and n-C_3H_7I are subjected to the (n,γ) reaction the ratio of specific activities CH_3I/C_3H_7I is 1.8, whereas for the $(n,2n)$ reaction with 14.1 Mev neutrons the ratio is 2.3 (*139*). Although the solutions were not de-aerated no scavenger was added, however, and this energy-dependent effect may not result from hot processes.

It has been found that some dependence of the organic retention on the recoil energy may exist in the solid phase, the $Br^{81}(n,\gamma)Br^{82}$ reaction in n-propyl bromide showing 93% retention as against 80% for the $Br^{79}(n,\gamma)$-Br^{80} and $Br^{79}(n,\gamma)Br^{80m}$ reactions (*91*). In the liquid state no significant differences in retentions were found between the three nuclear reactions. Later work confirmed that in the liquid n-propyl bromides there was no difference in retentions for these three (n,γ) reactions (*52, 263*), but indicated that differences were also absent for the solid phase (*263*).

When retentions from the $Br^{79}(n,2n)Br^{78}$ process in liquid and solid n-propyl bromide and isopropyl bromide, with and without Br_2 scavengers were compared with those from the $Br^{81}(n,\gamma)Br^{82}$ reaction, the retention of the 100,000 ev recoil Br^{78} was in all cases significantly greater than the $\sim$100 ev Br^{82} (*263*). It has been found in later work that the $(n,2n)$ reaction gives a greater organic retention for solutions of iodine in cyclohexane by comparison with the (n,γ) reaction, but no difference in retentions is observed for liquid n-propyl iodide (*262*). Neutron energy has been shown to have no effect on retentions in liquid n-propyl bromide, by using Sb-Be photoneutrons, Po-Be neutrons, cyclotron neutrons, and pile neutrons of differing degrees of moderation (*52, 263*).

Comparison of the Br^{80m}:Br^{80} isomeric transition with the $Br(n,\gamma)$

reactions rather strikingly demonstrates the fact that the products of hot reactions in liquid organic bromides do not depend upon the initial recoil energy supplied by the nuclear process. For example, the distribution of some 20 products in n-C_3H_7Br was found to be nearly identical for the I.T. and (n,γ) transformations (*84*). A similar situation is found for the two nuclear processes in solutions of bromine in CCl_4, C_6H_5F, C_6H_5Cl, and C_6H_5Br, the same relative yields of labeled products being produced by both transformations at all bromine concentrations (*137*, *323*). Plots of the organic retention versus free bromine concentration in both n-C_3H_7Br and i-C_3H_7Br are superimposable for activation by $Br^{80m} \rightarrow Br^{80}$, $Br^{79}(n,\gamma)Br^{80m}$ and $Br^{79}(n,\gamma)Br^{80}$ (*54*). In the case of the $Br^{79}(n,\gamma)Br^{80}$ and $Br^{80m} \rightarrow Br^{80}$ processes, reactions carried out with elementary bromine in pure hydrocarbons show the same increase of organic retention with chain length for both nuclear activations.

The general similarity between the effects of the bromine I.T. and (n,γ) reactions in organic liquids suggests that perhaps ion-molecule reactions are involved in the scavenger-insensitive retention-causing processes. We have seen that some contribution from ion-molecule reactions cannot be ruled out in the studies of the hot gas phase reactions of halogen and hydrogen atoms outlined in Section III,B,*1*. It is possible that charge neutralization processes may lead to fragmentation of organic molecules in a way similar to that caused by inelastic collisions. On the other hand it has been pointed out in Section I,A,*1* that charge neutralization may result in ~10–20 ev of kinetic energy being imparted to the pair resulting from the charge transfer reaction, and this may be sufficient to allow the Br atom to behave like a hot recoil towards the end of its track (*319*, *323*).

The retention of I^{131} in benzyl iodide after beta decay of Te^{131} in benzene solutions of dibenzyl telluride is depressed by addition of elementary iodine in a way resembling the effect of scavengers on the products of (n,γ) reactions in organic halides (*117*). The I^{131} atoms are here recoiling with energies of only ~2–4 ev and retention-causing reactions are presumably due to the charge and electronic excitation of the recoil. Interpretation is complicated in this system, however, because of the possibility of addition of iodine to the telluride.

Differences in organic retentions have been reported for the $Br^{79}(n,\gamma)Br^{80m}$ and $Br^{79}(n,\gamma)Br^{80}$ reactions in brominated alkyls (*39*, *40*, *41*, *43*). No differences have been found for the yields of Br^{80m} and Br^{80} in n-propyl bromides at low gamma doses (*52*, *248*), although the ratio of Br^{80m} and Br^{80} retentions can be caused to vary by allowing some radiolysis to occur with gamma doses in the range ~10^3–10^5 rads (*52*, *53*). The existence of an isomer effect in the presence of radiolysis products together with the use of relatively impure reagents in the earlier experiments in which an effect was found has suggested that the observed differences in retentions could have been due to the relatively higher probability of reaction with impurities by the isotopes or isomers of longer mean lives. In later work with irradiation times arranged so as to reduce differences in mean lives it has been found that in *n*-propyl bromide the Br^{80}/Br^{80m} ratio is changed by treatment with alumina using nonthermalized Ra/Be neutrons, whereas the ratio is unchanged for irradiations with thermalized neutrons (*6*). A similar finding has been made with the Br^{80m}/Br^{82} ratio (*7*). Attempts to verify these observations have not been successful (*323*).

Greater retentions of Br^{82} than Br^{80m} have been found in neutron-irradiated ethylene dibromide (*205*), but it was found to be difficult to obtain reproducible organic yields in this target (*205*, *269*), which suggests that impurities were not easy to eliminate, or that decomposition of this compound readily occurs to yield impurities with which the longer-lived Br^{82} has a greater chance of reacting (*205*).

On the whole the evidence of the previous paragraphs does not suggest that differences in retention of bromine isotopes or isomers occur as a result of differences in high-energy processes, but rather that the differences observed are due to reactions of thermalized Br atoms with impurities or decomposition products. This viewpoint is supported by the finding that the isotope effect in neutron-irradiated alkyl bromides can be suppressed by addition of allyl bromide (*22*), a known trap for thermalized Br atoms (*118*, *120*, *326*). No isotope effect has been found in the compounds CH_2Br_2 and C_2H_5Br (*202*, *218*) which do not readily decompose or form unsaturated compounds.

In the compounds CCl_3Br, CCl_2Br_2, CH_2ClBr, $CHCl_2Br$, and $CHClBr_2$ it has been found that the isotope effect for Br^{82} and Br^{80m} is independent of irradiation time and thus is not related to the mean lives of radioactive atoms in the target. The effect is independent of scavenger concentration but does not exist in the solid phase (*219*, *220*, *222*). This finding indicates a true high-energy isotope effect. In the series of chlorobromomethanes it has been found that the difference in retention, ΔR, between Br^{82} and Br^{80m} declines linearly with increase in the ratio of diffusive retention, R_0, to total retention (*219*, *222*), again indicating a nondiffusive isotope effect. In CH_2BrI, ΔR is in the opposite direction to that observed for the other bromo-compounds (*219*). In $CHBr_2F$ the usual ΔR effect is observed in liquid but not in solid phase (*222*).

It can be seen from the above paragraphs that there is rather conflicting evidence as to the role of initial recoil energy on the nondiffusive hot processes. In liquids nondiffusive isotope effects exist in the substituted methanes, but not in the propyl bromides, and in the halo-methanes the direction of the effect seems to depend on the composition of the target rather than on the initial recoil energy. With the present data it is difficult to draw firm conclusions, but rather convincing evidence for a relatively unimportant role of the magnitude of recoil energy imparted by the nuclear event comes from the closely similar effects of the (n,γ) and I.T. processes.

Relatively little work has been done so far to distinguish between hot and diffusive reactions of polyvalent recoils, although such work might be expected to throw light on the relative probabilities of forming one, two or three bonds in a localized hot process (*36*, *273*). It has been shown that P^{32} formed by the $S^{35}(n,\alpha)P^{32}$ reaction in neutron-irradiated solutions of CS_2 in benzene or chloro-benzene can replace hydrogen to form derivatives of mono-, di-, and tri-phenylphosphine (*221*). The curve of retention of As^{76} as monophenyl-arsenic versus $AsCl_3$ concentration in benzene after (n,γ) reaction shows a strongly $AsCl_3$ sensitive region, and an $AsCl_3$ insensitive region which declines linearly with increasing $AsCl_3$ concentration, in a very similar way to that for halogen scavengers in organic halides (*58*). $AsCl_3$ may be able to scavenge phenyl radicals either by direct chemical combination or as a result of Cl_2-yielding radiolysis in the pile, and this may be one of the reasons why the yield of phenyl-As^{76} compounds is considerably lower for irradiations of $AsCl_3$ in benzene than for irradiations of triphenylarsine in benzene (*37*, *273*). Furthermore addition of $AsCl_3$ to a solution of triphenylarsine in benzene depresses the phenyl-As^{76} yield (*272*). These findings suggest that As^{76} atoms recoiling in benzene are able to form bonds with phenyl radicals in a hot process, involving hydrogen replacement, or combination with a phenyl radical formed in an inelastic collision by diffusive or nondiffusive processes.

Using iodine and oxygen scavengers and dilution with "inert" solvents an attempt has been made to estimate the relative participation of hot and thermal processes in retention-causing reactions for the $As^{75}(n,\gamma)As^{76}$ process in triphenylarsine and the $P^{31}(n,\gamma)P^{32}$ reaction in tributylphosphate (*272*). The hot reactions have a dominant role in formation of organic mono-derivatives of both As^{76} and P^{32}, whereas thermal reactions are most important in the formation of tri-derivatives. The formation of di-derivatives is of an intermediate character. The findings suggest that a mono-derivative is first formed in a hot process, and that a diffusive process then leads to combination of the mono-derivative radical with a second or third organic radical to give the di- and tri-derivatives. Presence of oxygen or other radical scavengers tends to fix the recoil as the mono-derivative. There is evidence that in the case of P^{32} recoils the formation of the di-derivative can take place in the hot zone.

Studies with H^3 atoms activated by the $Li^6(n,\alpha)H^3$ process in liquids have considerably widened our views on the nature of hot reactions in the liquid phase (*129*, *247*, *251*). For liquid phase studies diphenyl picryl hydrazyl (DPPH) can be used as a radical scavenger (*234*), in addition to elementary halogens or oxygen.

In liquid methane or ethane the primary labeled compounds from H^3 recoil are HH^3 and the parent compound in roughly equal proportions, accounting for 88 and 79% of the H^3 activity respectively (*333*). The remainder of the H^3 is distributed among nonparent hydrocarbons, both saturated and unsaturated, with molecular size up to C_4 and greater. The similarity of the product distribution for the gaseous and liquid alkanes suggests that the retention-causing mechanisms outlined in Section III,B,*1* for gases may also be operative in the liquid phase (*251*). We may thus expect to find that direct displacement or abstraction reactions of the type of Eqs. (12) and (15) may be operative for H^3 recoils in liquids, and that cage effects and the physical condition of the medium may not influence the pattern of organic retention to the same extent as with recoiling halogen atoms.

Studies of the products of H^3 recoil in liquid ethyl and methyl alcohols and acetone (*251*) show that the greater part of the activity is present in the parent compound as shown in Table VI. The similarity in distributions of H^3 in acetone products, with or without DPPH, with the exception of —OH^3, again supports the conclusion that retention of H^3 in organic liquids is occurring mainly by a nondiffusive process.

TABLE VI
CHEMICAL STATE OF H^3 ATOMS REACTING WITH ALCOHOLS AND ACETONE (*251*)

Target / Product	Liquid C_2H_5OH	Liquid CH_3OH	Liquid CH_3COCH_3 No additive	Liquid CH_3COCH_3 DPPH added	Liquid CH_3COCH_3 Water added	Solid acetone
HH^3	51%	—	—	—	—	—
CH_3H^3	4%	—	—	—	—	—
CH_2H^3OH	1%	23%	—	—	—	—
$C_2H_4H^3OH$	22%	—	—	—	—	—
CH_3CH^3O	2%	—	9%	10%	8%	5%
$CH_3COCH_2H^3$	—	—	25%	22%	25%	24%
—OH^3	20%	29%	12%	22%	48%	17%

Degradation of the labeled acetaldehyde product from acetone showed that ~95% of the H^3 is present in the —CH^3O group, this compound being formed by the hot reaction:

$$CH_3COCH_3 + H^3 \rightarrow CH_3CH^3O + CH_3\cdot \qquad (28)$$

analogous to the alkyl group displacement reaction of Eq. (17). A similar mechanism probably accounts for the production of CH_2H^3OH from C_2H_5OH and CH_3H^3 from $CH_3{\cdot}CH_3$ (*333*).

The 2% yield of $CH_3{\cdot}CH^3O$ from C_2H_5OH in Table VI has been postulated to proceed via the usual H replacement reaction of Eq. (12), which in this case leaves an excited molecule:

$$CH_3{\cdot}CH_2{\cdot}OH + H^3 \rightarrow (CH_3CHH^3OH)_{\text{excited}} + H \tag{29}$$

$$(CH_3CHH^3OH)_{\text{excited}} \rightarrow CH_3\underset{|}{C}H^3OH + H \tag{30}$$

$$CH_3\underset{|}{C}H^3OH \rightarrow CH_3CH^3O + H \tag{31}$$

In support of this reaction sequence are the finding of aldehydes as frequent products of radiolysis or photolysis of alcohols (*179, 180, 229*) and the greater tendency for loss of H from the $—CH_2—$ rather than the $CH_3—$ group in gamma ray induced radiolysis or electron impact fragmentation of ethyl alcohol (*29*).

Studies have been made of the distribution of activity from H^3 recoils in a series of liquid carboxylic acids (*76*). The yields of activity in the parent-type molecules were independent of I_2 or O_2 scavengers, indicating hot processes. Diffusive reactions were those giving the small yields of molecules such as $C_2H_5H^3$ or $C_3H_7H^3$ from CH_3COOH, i.e., molecules having more atoms than the parent and thus not formed by direct hot reaction. This is a similarity with gas phase H^3 recoil systems (*77, 78*) in which "synthesis" products with more atoms than the parent were formed entirely by scavenger-sensitive reactions.

In the liquid carboxylic acids 99% of hot reaction products can be formed by breaking a single bond, which indicates a predominance of displacement reactions involving an atom or a group as in Eqs. (12) or (17). As in gases insufficient energy is coupled into the molecule to permit extensive fragmentation in most cases, and this applies despite the stiff wall of molecules backing the struck molecule in the liquid phase. There is a low yield of rearrangement or isomerization products, e.g., $(CH_3)_2CHCH_2CH_3$ and $(CH_3)_2CHCH_3$ from $CH_3(CH_2)_4COOH$ or $CH_3(CH_2)_3CH_3$ and $CH_3(CH_2)_2CH_3$ from $(CH_3)_2CH(CH_2)_2COOH$. This indicates that an activated complex with equilibrium distribution of energy is not being formed. Nevertheless, the yield of H^3-hydrocarbons resulting from decarboxylation is relatively high, suggesting that some residual energy after displacement may be transmitted along the molecule. A relatively high vulnerability of the —COOH group to direct displacement could, however, also explain this result (see, e.g., *142*).

In the liquid carboxylic acids there is an approximately linear relationship between the ratio HH^3/CH_3H^3 in the products and the ratio C—H bonds/C—CH_3 bonds in the target (*76*). This suggests that the amount of a given product in a hot displacement reaction depends largely on the fraction of total bonds which can be broken to give that product. Assuming that other steric or intramolecular factors do not complicate the issue it is possible to use such a simple "bond rupture probability" model to calculate the expected distribution of activity in the products from a given target molecule. There is found to be a reasonably good agreement between an activity distribution calculated on this basis for the liquid carboxylic acids and the distributions actually obtained. The deviations actually observed between the two distributions throw light on the relative importance of steric and intramolecular factors. For example, the observed yield of HH^3 is higher than theoretical, and there is a low yield of H^3 in labile form and in liquid products other than the parent acid. This suggests that C—H bond attack is relatively more probable than any other attack, a conclusion similar to that from the gas phase studies described in Section III,B,*1*. The higher yield of HH^3 than H^3-parent acid indicates that C—H bond attack favors abstraction rather than displacement. Furthermore HH^3 formation is found to be relatively more probable with secondary than with primary C—H bonds, a finding that can be related to the results of gas phase experiments discussed in connection with Eq. (25).

These studies have been extended to phenyl-acetic acid which was in liquid state during the irradiation (*75*). The amount of H^3 taken into the ring in this compound is greater than that incorporated into the side-chain (except for the carboxylic hydrogen), the specific activity of ring hydrogen being about 40 times greater than that of the methylene hydrogen. The more efficient labeling of aromatic than aliphatic groups also emerges from experiments with H^3 in solid *o*-toluic acid, in which the specific activity of a ring hydrogen is twice that of a methyl hydrogen, and from the observation that the hydrolysis of recoil H^3-labeled isopropyl benzoate yields benzoic acid with an H^3/H ratio more than three times greater than that of the isopropyl alcohol (*24*).

The behavior of C^{14} recoils in liquid systems has been studied in a number of recent works using the $N^{14}(n,p)C^{14}$ reaction with pile neutrons (*328, 329*).

When C^{14} atoms recoil in pentane radioactive hexanes are obtained. In one study the yields of *n*-hexane and 2-methyl-pentane were found to be in the ratio of 1.52/1 (*329*). This is very close to the ratio of 1.5/1 which would be found if hydrogen replacement by C^{14} is occurring on a statistical basis with equal probability for all H atoms. Similarly the ratio *n*-hexane/3-methyl pentane yield is 3.2/1, again close to the value of 3/1 for statistical replacement. Other experiments (*176*, *260*) have not yielded the expected ratios, the yields of *n*-hexane and 3-methyl-pentane being relatively higher than expected. It has been suggested that the presence of radiochemical impurities in the separated products may have accounted for the discrepancies. Statistical replacement of H by C^{14} in toluene to produce the xylenes and ethyl benzene has also been observed (*329*).

The data on the whole suggest that C^{14} recoils are able to replace H atoms in aliphatic chains or aromatic rings with a fairly equal probability for each hydrogen position. The reaction could be a direct displacement reaction of the type of Eq. (12). Alternatively a bare C^{14} atom may be stopped in a head-on collision with a C atom bound in a molecule in the high energy region of the recoil process, and may then abstract H atoms from molecules in the solvent cage walls forming a $C^{14}H_3\cdot$ radical and creating organic radicals with which the labeled species would then combine (*176*).

It has been shown that C^{14}-toluene is formed when C^{14} atoms recoil in liquid benzene in the presence of DPPH or 1,3,5-trinitrobenzene as radical scavengers (*294*), so that in this case a nondiffusive hot process is involved. Experiments have been done using various mole fractions of different amines as nitrogen sources for the (*n*,*p*) reaction in benzene. It has been found that the C^{14}-toluene yield depends on the availability of hydrogen from the nitrogenous compound (*329*). This result supports the picture of hydrogen abstraction to form a $C^{14}H_3\cdot$ radical prior to the retention-causing reaction, although this radical might conceivably be formed and interact with a benzene ring in a second high-energy collision rather than after thermalization of the recoil.

C^{14} can also replace C or N atoms in molecules of the medium in which recoil occurs. Both statistical and nonstatistical behavior have been observed.

In aromatic systems the percentage of C^{14} retentions per C or H position in the molecule are very similar (*329*), showing that the replacement reaction yields depend primarily on the relative probability of striking a C or H atom in the molecule and not on the mass of the replaced atom. This is a difference from the case of Br recoils in mono-halogenated benzenes, described earlier, in which more efficient energy transfer in atom-atom collisions seems to lead to higher organic retentions. The simple statistical picture with C^{14} recoils does not apply in all cases, however, since C replacement from the CH_3-group in toluene to yield C^{14}-toluene occurs with considerably greater probability than the formation of the same product by NH_2- replacement in aniline, despite the similar masses of the N and C atoms (*329*).

Although calculations of specific activities expected per C or H atom or the relative yields of various products can yield some information on the relative frequencies of location of the initial point of attack at different molecular sites, degradation of the products to ascertain C^{14} distribution is required to illuminate intramolecular rearrangements. The distribution of radioactivity between methyl carbon and ring carbons in the case of C^{14}-toluene, formed by NH_2- replacement in aniline, resembles quite closely the distributions for C^{14}-toluene formed by H replacement in benzene, for C^{14}-*o*-xylene from toluene by H replacement or for C^{14}-toluene prepared from toluidines formed by aniline ring H replacement. This perhaps indicates a common intermediate. On the whole C replacement by C^{14} in simple aromatic compounds seems to result in only moderate deviations from statistical behavior in both liquid and solid phase.

In the case of aliphatic compounds less work has been done in the liquid phase. The replacement of H by C^{14} recoils in pentane and methanol has been found to be twice as probable as C replacement in the chain (*329*).

The experiments with C^{14} recoils have already served to show that the mass of the replaced atom or group in the molecule does not have much influence on the probability of C^{14} retention. They also show that completely random and uniform labeling does not occur, nor does completely specific labeling. In all cases isotope distributions in the products show that some intramolecular process results in redistribution of the C^{14} after its incorporation into the molecule. Chemical effects are thus of considerable importance in the pathways leading to the final products and lead to marked deviations from strictly statistical behavior. Considerable differences from statistical distribution have been observed with C^{14} recoils in solid systems in work not reviewed here (*25*, *30*, *96*), although in some solids the predictions of statistical replacement have been fairly closely fulfilled (*216*, *330*, *342*).

C. THERMAL OR DIFFUSION-DEPENDENT REACTIONS AFTER NUCLEAR ACTIVATION AND RADIATION EFFECTS

In this review attention has been concentrated on the high-energy interactions resulting from nuclear activation, since this field represents the strongly specific contribution of the nuclear technique to the subject of chemical reactions. Nevertheless, a considerable volume of work has been done to elucidate the chemical behavior of the radioactive atoms when they have reached thermal energies, which can only be partially indicated here.

In liquids the study of diffusive reactions may throw light on the way in which radical nests are generated along the recoil track, and possibly on the distribution of the various types of radicals produced in inelastic collisions as a function of track length traversed and thus of recoil energy at the moment of collision.

Diffusive reactions yield mainly parent-type molecules in neutron-irradiated liquid ethyl bromide and ethylene bromide (*202, 205*). Extensive analysis of diffusive reaction products in liquid *n*-propyl and isopropyl bromides has been done (*54*), and indicates once again the predominance of parent-forming reactions and the relative absence of reactions involving radicals produced by extensive molecular fragmentation. A similar picture is found for CH_3Br and CH_2Br_2 (*127*).

No correlation has been found between bromine content of target molecules and relative participation of diffusive processes in reactions leading to organic retention, but the diffusive retention seems to rise with number of H atoms (*220*). This may be related to the suggestion made in Section III,B,*2* in connection with the saturation effect for the ratio R_E/R_{total}, namely that increase in the number of halogen atoms per target molecule may increase the probability of local generation of elementary halogen scavenger.

Diffusive retention depends on the way in which radicals will diffuse away from the recoil track. Various theoretical approximations have been made to solve the appropriate diffusion equation (*68, 157, 193, 204, 256*) and have been successfully applied to diffusive reactions in neutron-irradiated aliphatic bromides (*204*), bromo-methanes and chloro-bromomethanes (*220*).

Radiation effects may have a considerable influence on the course of diffusive reactions as various radiolysis products become available for reaction with the thermalized radioactive atoms. This effect can be calculated (*167*) and demonstrated (*248*) to be sometimes of little importance with low gamma intensity neutron sources. Even here, however, thermalized radioatoms may react with organic radicals produced by radiolysis in the course of the irradiation (*53*, *167*).

When nuclear reactors are used as neutron sources the intense gamma fields may sometimes induce a considerable fraction of the target to undergo radiolysis. When as much as several percent of the target has suffered decomposition hot processes may be affected as well as diffusive reactions. For example, when C^{14} recoils react with a sample of NH_3 gas receiving $\sim 10^8$ rads of gamma radiation, a high yield of $C^{14}H_4$ is observed even in the presence of inert gas moderators (*338*). When C^{11} recoils are used in a low radiation field, however, no $C^{11}H_4$ production is observed (*184a,b*).

Different compounds may have markedly different radiation sensitivities. For example, Cl^{38} retention in the radiolysis-resistant *n*-propyl chloride remains fairly constant up to a total pile gamma dose of $\sim 10^7$ r, while in *n*-propyl bromide a marked increase in retention occurs after 10^4 r, probably due to HBr^{80} reaction with propyl radicals and propene molecules produced by radiolysis (*286*). Gamma radiation may also induce molecular isomerization, the formation of isopropyl chloride from *n*-propyl chloride being a linear function of the gamma dose received in the reactor (*286*).

The reactions undergone by H^3 recoils in gas phase and liquid systems may be highly sensitive to radiation effects. Heavy particle bombardment by the recoil tritons, alphas or protons from neutron reactions with He^3 or Li^6 may induce radiation damage in both target molecules and already formed radioactive species. Many radiation effects are reported in the papers referred to in discussing H^3 recoil reactions in Sections III,B,*1* and III,B,*2* (e.g., *67*, *161–163*, *247*, *258*, *317*, *318*).

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List of Symbols

α	Logarithmic energy decrement for elastic collisions
A_i	Radioactivity of product *i* of hot reaction
A_s	Radioactivity of all reaction products
e	Charge of electron
E_b	Bond energy
E_β	Energy of emitted beta particle
E_i	Bond activation energy
E_{int}	Internal energy of a polyatomic molecule
E_{γ_0}	Net gamma energy required for bond rupture
E_r	Rotational energy
E_R	Recoil energy
E_T°	Net recoil energy necessary for bond rupture
f	Probability of collision between hot atom and molecule
I_{exc}	Lowest electronic excitation level
I_i	Definite integral involving $p(E)$, Eq. (10)
I_n	Nuclear angular momentum
K_i	Definite integral involving $p(E)$, Eq. (11)
m	Mass of recoil atom
M	Molecular weight
m_c	Mass of atom C in polyatomic molecule
m_e	Mass of electron
m_i	Mass of *i*th atom in polyatomic molecule
N_{Br}	Mole fraction bromine
N_s	Mole fraction scavenger
$p(E)$	Energy-dependent reaction collision efficiency or distribution of excitation energies
$P_D(E)$	Probability of molecular dissociation
R_E	High energy retention
Π	Nuclear parity
Q	Momentum impulse
r	Distance between nuclei or charge centers
$\mathbf{r}_i$, r_i	Position vector for *i*th atom in a polyatomic molecule
V	Potential energy

v_i	Vibrational velocity of *i*th atom in a polyatomic molecule
Z	Nuclear charge
$\boldsymbol{\omega}$, ω	Angular velocity
Ω	Obstruction parameter for H^3 collisions with molecular H atoms

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