The Aqueous Phase Oxidation of Cyclohexane using Gamma Radiation

RONALD C. ASHLINE and ROBERT L. VON BERG
Cornell University, Ithaca, New York

A study was made of the radiolytic oxidation of cyclohexane in aqueous solution by using cobalt 60 gamma radiation. In the presence of dissolved oxygen gas the reaction proceeds irreversibly with the formation of a number of oxidation products. Those identified were cyclohexanol, cyclohexanone, and hydrogen peroxide. Trace quantities of carbon dioxide were also detected in the liquid phase. Using a constant dose rate of 15 × 10^4 rad./hr. in all runs, radiation yields were $G(C_6H_{11}OH) = 0.49$, and $G(C_6H_{10}O) = 1.08$. When molecular oxygen was excluded from the system, neither cyclohexanol nor cyclohexanone was formed on irradiation. A simplified kinetic model based on competition by the various solutes in the system for a single primary radical species produced by radiolysis of the solvent molecules is developed. Results generated using the mathematical model are compared with the experimental data. Excellent agreement between the observed and computed trends is noted at radiation doses up to 50 × 10^4 rad.

In the radiolysis of dilute aqueous solutions that uses gamma radiation, the greatest amount, by far, of radiation absorbed in the system is the radiation which interacts with the solvent molecules. This is a result of the nonspecific nature of the absorption of gamma rays by different molecules and the preponderance of water molecules in such systems. When the ionizing radiation interacts with water, a net production of hydrogen atoms and hydroxyl radicals result from a series of intermediate reactions that begin with the formation of the H_2O^+ ion (*1*). These atoms and radicals will undergo radical-molecule reactions with dissolved substances to form one or more products. This series of events beginning with the absorption of energy by solvent molecules and terminating with the conversion of solute molecules is referred to as the *indirect action* of radiation, that is, the appearance of an effect on a minor constituent of a mixture which results from energy deposition in the major constituent.

The radiolysis of dilute aqueous solutions of organic compounds has been the subject of numerous investigations in recent years. Most systems that were studied have been ones in which the solubility of the organic compound is appreciable. In this category, the conversion of benzene to phenol has received considerable attention due to the high energy yield of phenol that results under certain irradiation conditions and the resulting possibility of commercial significance. Comprehensive studies of the system include those of Phung and Burton (*12*), and Proskurnin et al. (*13*). More recently, the same system was studied by Engquist and Martin (*7*) who obtained even higher energy yields than had previously been reported, by working with agitated water-benzene solutions.

In regard to the radiation chemistry of compounds that exhibit very low solubility in water, a very limited amount of information has been published. This is due, in part, to the enormous difficulties that arise in analyzing for minute quantities of organic materials in aqueous solutions. Thus, work with aqueous solutions of saturated hydrocarbons has been minimal. Johnson and Weiss (*11*) formed methylhydroperoxide with a yield $G(CH_3OOH)$ of 0.5 on irradiating neutral solutions containing methane and oxygen gases. The only other report which this author found on saturated hydrocarbons was a mention by Phung and Burton (*12*) of two experiments on solutions of cyclohexane. They reported a hydrogen yield $G(H_2)$ of about 3, indicating that all hydrogen atoms reacted with cyclohexane by hydrogen abstraction. These authors made no mention, however, regarding the fate of the resulting cyclohexyl radicals.

Although various authors have dealt with the kinetics of radiation-chemical reactions from a theoretical viewpoint (*1, 4, 18, 19*), few authors have included in their discussions comparisons with actual data. In the present paper, the radiolysis of cyclohexane in water to form the intermediate oxidation products, cyclohexanol and cyclohexanone, is approached from a kinetic viewpoint. Based on the observed findings that are presented, a kinetic model of the system is developed. Comparisons between the calculated results and the experimental data are shown.

Ronald C. Ashline is with Allied Chemical Corporation, Morris Township, New Jersey.

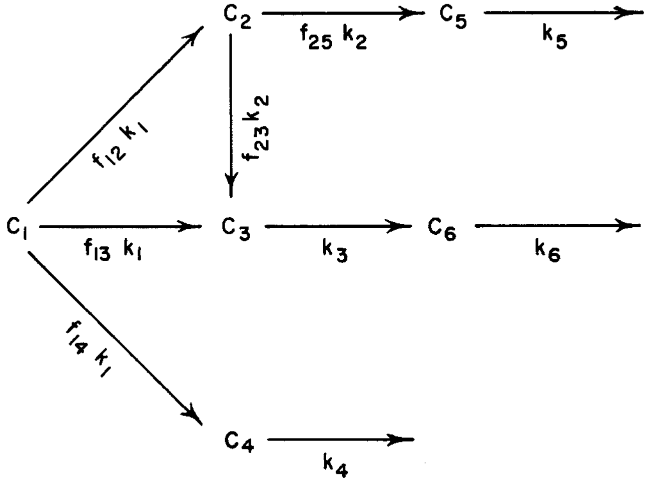

Fig. 1. Reaction scheme.

EXPERIMENTAL PROCEDURE

The apparatus consisted of a glass lined 2,000 ml. capacity Model 4501 Parr pressure reaction apparatus. The reactor was constructed of stainless steel and incorporated a sealed motor-driven stirrer. The apparatus was surrounded by a source holder which supported up to twenty cylindrical gamma-radiation sources in a circular arrangement. Each source contained a nominal value of 500 curies of cobalt 60. The entire apparatus was contained in a shielded cave. Operation of the equipment was performed remotely with the use of a pair of master-slave manipulators.

The standard charge to the reactor was 1,500 ml. of solution containing various amounts of cyclohexane, cyclohexanol, and cyclohexanone. In the experimental run, in which the solution was saturated with respect to cyclohexane throughout the entire length of the run, approximately 7.5 g. of cyclohexane was added to 1,500 ml. of distilled water contained within the reactor. In preparing aqueous solutions of cyclohexane that contained less than that amount required to saturate the solution at room temperature and atmospheric pressure, the cyclohexane was injected just above the liquid surface from a 0.5 ml. capacity syringe graduated in 0.01 ml. subdivisions. The exact quantity of cyclohexane placed in the reactor was determined by weighing the syringe before and after injection. During operation of the reactor, the head space above the liquid surface was pressurized with oxygen gas and the stirrer driven at a speed of approximately 550 rev./min.

Experimental runs were carried out at room temperature and under an oxygen pressure of 18.7 lb./sq. in. abs. One run was carried out in the absence of dissolved oxygen. In this single run, the system was purged with nitrogen gas prior to the addition of cyclohexane and the solution was maintained under a nitrogen pressure of 15.7 lb./sq. in. abs. during the reaction period. An energy absorption rate of 15×10^4 rad./hr. was used in all runs. The standard Fricke method of chemical dosimetry with a G-value for the ferrous to ferric sulfate reaction of 15.5 was employed to measure the dose of gamma radiation absorbed by the system.

Liquid samples were withdrawn from the reactor at selected intervals during a run and were stored in stoppered Pyrex tubes. The samples were placed behind a lead barrier within the gamma radiation cave until the cobalt sources were returned to their storage wells at the conclusion of each run.

Concentrations of reactants and products were determined by gas chromatographic analysis of the aqueous samples. Samples were analyzed by using an Aerograph Model 600-C chromatograph equipped with a hydrogen flame ionization detector. Sample analysis was carried out with a 6 ft. × ⅛-in. stainless steel column packed with 60/70 mesh GAS-CHROM Z coated with 10% Carbowax 20M terminated with terephthalic acid. The column was operated at 105°C. with nitrogen carrier gas. Retention times for cyclohexane, cyclohexanone, and cyclohexanol were 46 sec., 4 min. 20 sec., and 6 min. 20 sec., respectively. Further details of sampling and analysis are given elsewhere (*3*).

RESULTS AND DISCUSSION

Oxidation Products and Reaction Scheme

Irradiation of a dilute aqueous solution of cyclohexane in the presence of dissolved oxygen causes the formation of a number of oxidation products. These oxidation products, which were identified in the liquid phase, include cyclohexanol, cyclohexanone, hydrogen peroxide, and trace amounts of carbon dioxide. Continued irradiation results in the eventual destruction of the intermediate compounds, cyclohexanol and cyclohexanone, as they in turn become converted to higher oxidation products. These latter compounds were not detected by gas chromatographic analysis. In the absence of dissolved oxygen neither cyclohexanol nor cyclohexanone are formed.

The conventional thermal liquid phase air oxidation processes for converting cyclohexane to the intermediate oxidation products, cyclohexanol and cyclohexanone (*2*, *5*, *16*), and the radiation-chemical reaction are analogous in the sense that both proceed through a complex of radical reactions although the initiator is different for the two cases. In the thermal process, cyclohexanone or a peroxide type initiator is commonly used. Higher oxidation products formed include adipic acid and other dicarboxylic acids with shorter hydrocarbon chains. In the radiation process, H· and ·OH radicals produced by radiolysis of water molecules initiate the oxidation reactions. Adipic acid is not formed in detectable amounts.

The radiolytic oxidation of cyclohexane in aqueous solution occurs as a series of simultaneous and consecutive irreversible reactions. Cyclohexane is converted simultaneously to cyclohexanol, cyclohexanone, and to one or more products which were not identified. Cyclohexanol in aqueous solution is partially converted to cyclohexanone during irradiation, thus providing a second path by which the latter intermediate product is formed. Cyclohexanone in turn is converted to higher oxidation products. The reaction sequence is shown in Figure 1. This reaction scheme is a modified version of that employed by Spielman (*15*) in developing a kinetic model to correlate batch laboratory and continuous stirred reactor pilot unit data for the boric acid modified air oxidation of cyclohexane. C_4, C_5, and C_6, representing concentrations of unidentified products formed in the system, are included to satisfy a material balance on the system.

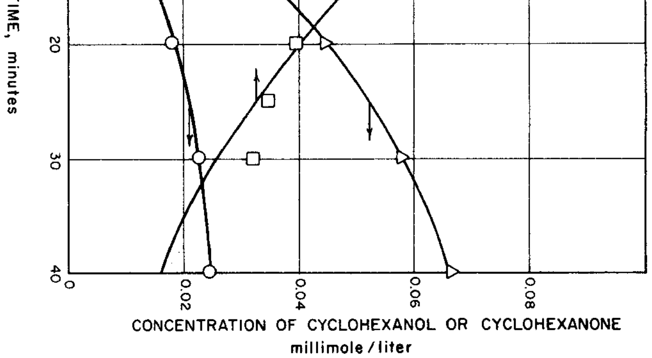

Fig. 2. Cyclohexane oxidation. ☐ cyclohexane, ○ cyclohexanol, △ cyclohexanone. The curves are the theoretical predictions based on the kinetic model developed in this paper.

Comparison of Experimental Data with Numerical Solutions of Kinetic Model

Figure 2 shows a plot of the concentrations of cyclohexane, cyclohexanol, and cyclohexanone vs. irradiation time. The experimental data points appearing in this figure and in subsequent figures are compared with mathematical solutions of the kinetic model developed later in this paper. In this run, the initial concentration of cyclohexane present in the solution charged to the reactor (0.840 millimole/liter or 0.0706 g./kg. water) compares closely with the saturation concentration of 0.06 to 0.08 g./kg. water reported by Irmann (*10*).

Observation of the experimental data in Figure 2 reveals that cyclohexanol and cyclohexanone, both initially absent from the reaction system, are formed simultaneously by the radical attack of cyclohexane during the irradiation of oxygenated solutions of the cyclic hydrocarbon. These products which are formed with the yields, $G(C_6H_{11}OH) = 0.49$ and $G(C_6H_{10}O) = 1.08$, account for approximately 16% of the cyclohexane that disappears. The reader's attention is directed to the different ordinate scales used in expressing the concentrations of the three components shown in Figure 2. Other products formed directly from cyclohexane which are required to satisfy a material balance were not detected by gas chromatography. These unidentified products probably consist of highly polar oxygen-containing molecules, for example, aliphatic hydroxy acids, hydroperoxides, etc. The failure of these compounds to produce any detector response is attributed to their being held irreversibly on the chromatographic column. These products are grouped together and designated as C_4 n Figure 1.

Prolonged irradiation would result eventually in the complete destruction of the cyclohexanol and cyclohexanone as these compounds are converted to higher oxidation products. This behavior is typical of systems in which an intermediate product reacts with one or more components of the system. Examples of this behavior may be found in many oxidation reactions where the desired intermediate product is converted to unwanted degradation products if the reaction is allowed to continue beyond an optimum degree of conversion. This effect cannot be seen in Figure 2, however, since the system was not irradiated for a sufficient length of time for maxima to occur in the data for the production of cyclohexanol and cyclohexanone.

Figure 3 shows a plot of the concentrations of cyclohexanol and cyclohexanone vs. irradiation time that resulted when a solution which initially contained 0.400 millimole/liter of cyclohexanol was irradiated. The absence of cyclohexane as a reaction product indicates that the conversion of cyclohexane to cyclohexanol and higher oxidation products proceeds irreversibly under the action of gamma radiation. During the irradiation of aqueous solutions of cyclohexanol, only 17% of the reacted alcohol was converted to the desired product, cyclohexanone. Other products formed from the alcohol were not detected. The reader's attention is again directed to the different ordinate scales used for the two compounds.

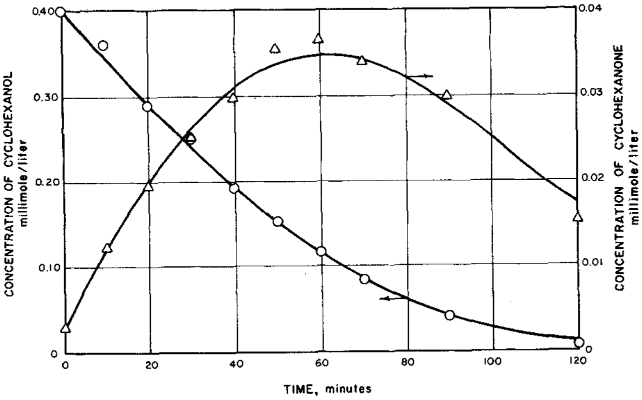

Fig. 3. Cyclohexanol oxidation. ○ cyclohexanol, △ cyclohexanone. The curves are the theoretical predictions based on the kinetic model developed in this paper.

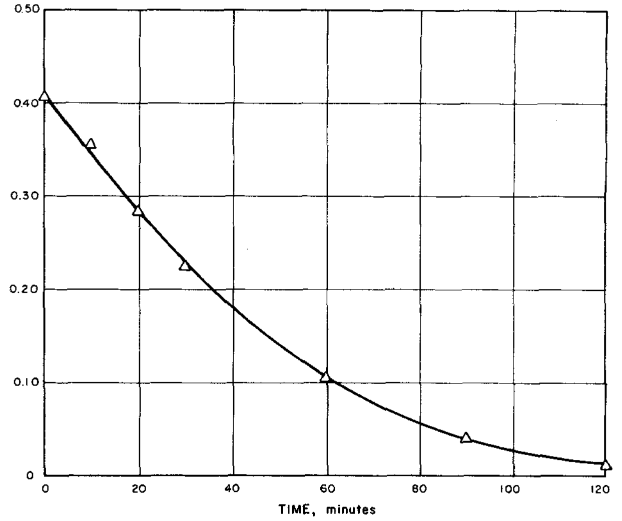

Fig. 4. Cyclohexanone oxidation. △ experimental data. The curve is the theoretical prediction based on the kinetic model developed in this paper.

The fact that cyclohexanone is an intermediate product in the reaction sequence is clearly in evidence in Figure 3. During the early stages of the reaction, the concentration of cyclohexanone increases as a fraction of the alcohol is converted to the ketone. As the reaction continues, both the remaining alcohol and the ketone that is formed compete for the free radicals that arise from the radiolysis of the water molecules. Eventually the point is reached where the rate of formation of the ketone equals its rate of disappearance. This point corresponds to the maximum in the curve for the production of the ketone. As the reaction proceeds further, the concentration of the ketone decreases as it becomes converted to higher oxidation products.

The maximum concentration of ketone formed is dependent on a number of factors. These include the initial concentration of the parent compound in addition to the relative rate constants characterizing the reactions between the various molecular components of the system and the radicals that are formed by the radiolysis of water molecules.

In Figure 4, the concentration of cyclohexanone is plotted vs. irradiation time for a system initially containing 0.407 millimole/liter of cyclohexanone. The graph shows a continuous decrease in concentration that occurs as the cyclohexanone reacts with the radiolysis products of the medium. The fact that neither cyclohexanol nor cyclohexane is produced provides further evidence of the irreversible nature of the reactions shown in Figure 1. The products of the reaction were not detected by gas chromatography.

Figure 5 shows a plot of the concentrations of cyclohexanol and cyclohexanone vs. time formed in a solution continuously saturated with respect to cyclohexane. No alcohol or ketone was initially present. As the reaction proceeds, steady state concentrations of the alcohol and ketone are approached. This is apparent from the fact that the slopes of the curves approach zero at long irradiation times in contrast to the behavior noted in Figure 3 which shows the concentration of cyclohexanone passing through a maximum. This behavior is readily ex-

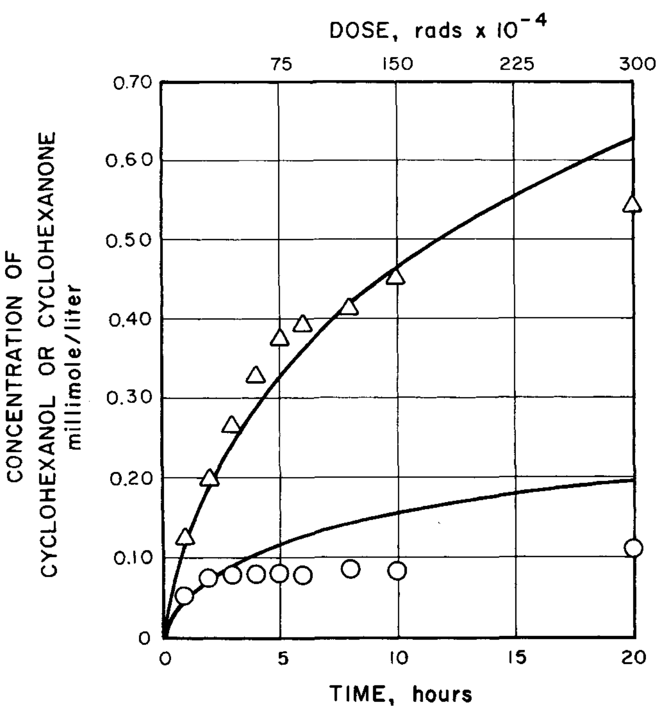

Fig. 5. Cyclohexanol and cyclohexanone formation in a continuously saturated aqueous solution of cyclohexane. ○ cyclohexanol, △ cyclohexanone. The curves are the theoretical predictions based on the kinetic model developed in this paper.

plained by the fact that the rates of formation of alcohol and ketone remain nearly constant as long as the solution remains saturated with respect to cyclohexane, whereas their rates of disappearance increase with concentration.

As the concentrations of alcohol and ketone build up in the solution, they react with an increasing fraction of the H· and ·OH radicals that are formed by the radiolysis of water molecules. This results in an increase in the rate at which these intermediate reaction products are converted to higher oxidation products. The point is eventually reached at which the rates of formation and disappearance become equal. This equality establishes the steady state concentration of each component. If the reaction were continued to the point where the system became depleted with respect to cyclohexane, the concentrations of cyclohexanol and cyclohexanone would then decrease, eventually disappearing altogether.

As is characteristic of this type of system in which the desired intermediate product undergoes further reaction to form unwanted byproducts, the fractional conversion of cyclohexane to cyclohexanol and cyclohexanone is highest at the outset. The selectivity decreases steadily as the reaction continues.

Kinetics of Radiation-Chemical Reactions

The preceding results can be explained in terms of a radical-diffusion model (*8*, *9*, *14*). According to this model, irradiation of the medium results in the production of hydrogen atoms (or solvated electrons) and hydroxyl radicals that diffuse from the regions in which they are born into the bulk of the solution. Although radical recombination reactions forming molecular-hydrogen, hydrogen peroxide, and water occur to a limited extent, the bulk of these reactive species ordinarily disappear by reaction with dissolved materials present in the solution. These latter reactions are responsible for the formation, among other things, of the molecular products that are observed.

As a consequence of the large velocity constants that are characteristic of radical-molecule reactions, the rate controlling step in the formation of the final molecular products is the decomposition of the medium into H· and ·OH radicals. Since the rate at which these are formed is proportional to the radiation intensity, the rate at which a single solute reacts is independent of the concentration of that solute. This was confirmed experimentally using aqueous solutions of cyclohexanone by observing that the initial rate at which the concentration of solute decreased during irradiation was independent of solute concentration.

If two different solutes, *A* and *B*, are present each of which may react with the same radical and the second-order velocity constants for these reactions are k_A and k_B, then the relative probability that a given radical will react with *A* rather than with *B* is the ratio of the two products $k_A[A]$ and $k_B[B]$, where the symbols enclosed in brackets represent concentrations of the respective solutes. The kinetics of multicomponent systems may be treated in an analogous manner. Apart from chain reactions which were not observed in the present study, the kinetics of radiation-chemical reactions in ordinary solutions are determined only by competition of the different solutes in a given system for the radicals formed by the radiolysis of the solvent molecules.

FORMULATION OF THE KINETIC MODEL

The following kinetic relations which have been derived for the radiolytic oxidation of cyclohexane in aqueous solution are based on the reactions of a single primary radical which is hypothesized to be formed when gamma radiation interacts with solvent molecules. The relative rate constants of second-order reactions between the primary radical and competing solutes determine the course followed in the conversion of cyclohexane to intermediate oxidation products. In the development below, it is assumed that six solutes, a primary radical, and diluent comprise the reacting system.

Basic Equations

The rate of disappearance of the reactive species $r\cdot$ by reaction with the *i*th solute is given by the second-order rate expression

$$(-dr\cdot/dt)_i = k_i C_i r\cdot \tag{1}$$

If it is assumed that each radical $r\cdot$ that reacts in accordance with Equation (1) results in the disappearance of α_i molecules of the *i*th component by a series of consecutive intermediate steps, then it follows that

$$r_i = \alpha_i\,(-dr\cdot/dt)_i \tag{2}$$

Setting the total rate of disappearance of $r\cdot$ by reaction with the six components considered equal to the rate of formation of $r\cdot$, one gets for the stationary state:

$$\sum_i (-dr\cdot/dt)_i = R^* \tag{3}$$

Combination of Equations (1) and (3) and rearrangement of terms leads to the following expression for the stationary radical concentration:

$$r\cdot = R^*/\sum_i (k_i C_i) \tag{4}$$

Substituting this expression for $r\cdot$ into Equation (1) and letting $K_{1i} = k_1/k_i$, one obtains the relationship

$$(-dr\cdot/dt)_i = [(C_i/K_{1i})/\sum_i (C_i/K_{1i})]R^* \tag{5}$$

Finally, combining Equations (2) and (5) and observing that $\alpha_i R^* = R_i$, one obtains the desired rate expression

$$r_i = [(C_i/K_{1i})/\sum_i (C_i/K_{1i})]R_i \quad (6)$$

Equation (6) states that the rate of disappearance of each solute in a solution containing six reactive solutes equals the weighted mole fraction of the component multiplied by the rate at which that component would disappear if it were the only solute present in the system.

With reference to Figure 1, it is apparent that the net rates of formation of the three components of major interest are given by the following equations:

$$dC_1/dt = -r_1 \quad (7)$$

$$dC_2/dt = f_{12}r_1 - r_2 \quad (8)$$

$$dC_3/dt = f_{13}r_1 + f_{23}r_2 - r_3 \quad (9)$$

Using the symbols, C_4, C_5, and C_6, to denote the combined concentrations of each of the three unidentified components shown in Figure 1 and the degradation products that are derived from each of them, one may also write the following three equations:

$$dC_4/dt = f_{14}r_1 \quad (10)$$

$$dC_5/dt = f_{25}r_2 \quad (11)$$

$$dC_6/dt = r_3 \quad (12)$$

A material balance requires that

$$f_{12} + f_{13} + f_{14} = 1 \quad (13)$$

and that

$$f_{23} + f_{25} = 1 \quad (14)$$

Assumptions

The basic assumptions made in developing the foregoing kinetic model, solving the equations, and applying the results to the isothermal radiolytic oxidation of cyclohexane in aqueous solution are the following:

1. All reactions that occur are irreversible in nature. This assumption is supported by a standard thermodynamic analysis of the oxidation reactions which indicates equilibrium constants strongly favoring oxidation products. Although radiation will affect equilibrium when reactants and products are attacked directly by the radiation, such is not the case here. While the reactions under consideration involve radicals produced from the water by radiation, the organic reactants and products are not themselves directly affected to any large extent by the radiation. Thus, a standard thermodynamic analysis should provide a good indication of the actual equilibrium. This assumption is further supported by the fact that no experimental evidence of reversible reactions was observed when aqueous solutions of pure cyclohexanol or cyclohexanone were irradiated.
2. The radiolysis products of water, H· and ·OH, are treated as being equivalent radicals. In the foregoing development, they are represented as the single primary radical, $r\cdot$.
3. The fraction of the radicals, H· and ·OH, recombining within the spurs in which they are formed in high localized concentrations is considered to be independent of solute concentration. Thus at a given dose rate the number of radicals which succeed in diffusing into the bulk of the solution remains constant over a given period of time.
4. The radicals which diffuse into the bulk of the solution react with solutes that are present rather than combining with each other. Since the rate constants for radical recombination reactions are of the order of 10^9 liters/(mole-sec.) (*6, 17*), dose rates on the order of 10^5 rad./hr. can lead to radical concentrations of 10^{-7} g.moles/liter at most. Thus these radicals are not likely to react with each other when reactive solutes are present in concentrations of 10^{-5} g.moles/liter or more.
5. H· and ·OH radicals are not regenerated in any of the intermediate steps leading to the formation of the molecular products. This assumption is supported by the lack of any indication of a chain reaction occurring.
6. Stationary concentrations of the radicals, H· and ·OH, are formed in solution after a very brief period of irradiation. Since there must exist a finite difference between the rates of radical formation and disappearance, however, to enable $r\cdot$ to vary as required by Equation (4), this assumption implies that the rate at which $r\cdot$ changes with time is small compared to the rates of radical formation and consumption. These conditions would normally prevail in the case of radical-molecule reactions where rate constants are typically large.
7. The unidentified products, C_4, C_5, and C_6, and all degradation products which derive from them are treated as reactive solutes. In the absence of any knowledge of their true values, the rate constants associated with the disappearance of the degradation products that derive from C_4, C_5, or C_6 are equated to the rate constant characterizing the rate of disappearance of the parent compound.
8. The number of moles of oxidation products formed is equal to the number of moles of feed reacted. Thus the number of moles contained within the reactor remains constant regardless of the degree of conversion. This assumption implies either that no cleavage or condensation of oxidized material takes place, or else that the number of moles which appear, owing to cleavage, is equal to the number of moles disappearing as the result of condensation.
9. In simulating runs carried out under conditions where the quantity of unreacted cyclohexane is in excess of the amount required to saturate the water phase, a solution of the equations is obtained by holding the concentration of cyclohexane constant at the saturation value. This implies that the presence of the oxidation products in solution does not alter the solubility of the hydrocarbon and that the presence of excess cyclohexane in the form of dispersed droplets does not result in an increased effective concentration of that component. This also implies that the rate at which reacted cyclohexane molecules in the water phase are replenished with unreacted cyclohexane is not diffusion limited, since the bulk concentration of the latter would thereby be diminished below the saturation value.
10. The concentration of dissolved oxygen influences each of the reactions to the same extent and is uniform throughout the reactor. Thus it may be combined with the true rate constants yielding effective rate constants. Handling the oxygen concentration in this manner avoids making any assumption as to the reaction order with respect to oxygen. However, runs at different oxygen pressures most likely would not be comparable.

Evaluation of Parameters

The various parameters (R_i, f_{ij}, K_{1i}) appearing in the foregoing kinetic equations, with the exception of K_{14}, K_{15}, and K_{16}, were calculated from initial reaction rates. The evaluation of these latter three parameters is impossible without a knowledge of the compounds that are involved. Consequently, values were assigned to these three parameters which achieved the best comparison between the computed results and the experimental data. Experimentally determined values of the parameters along with the actual values used in computing the theoretical solutions appearing in Figures 2 to 5 are given in Table 1. All values listed apply specifically to the radiolytic oxidation of cyclohexane, cyclohexanol, and cyclohexanone at 25°C. and 18.7 lb./sq.in.abs. oxygen pressure using a gamma radiation dose rate of 15×10^4 rad./hr.

TABLE 1. VALUES OF THE KINETIC PARAMETERS

Parameter	Average experimental value*	Value used in mathematical solution of rate equations
f_{12}	0.050 ± 0.001	0.043
f_{13}	0.112 ± 0.003	0.105
f_{23}	0.174 ± 0.023	0.175
K_{12}	1.68 ± 0.18	1.5
K_{13}	2.41 ± 0.44	3.0
K_{14}	—	1.5
K_{15}	—	5.0
K_{16}	—	7.5
R_1	0.0240 ± 0.0018	0.028
R_2	0.00591 ± 0.00011	0.0059
R_3	0.00668 ± 0.00018	0.0067

* Limits shown were obtained from duplicate runs.

R_i was determined directly by measuring the initial rate at which C_i decreased in a solution containing only the pure solute. The values of f_{ij} were obtained by dividing the rate of formation of product j by the rate of disappearance of component i from a solution of the pure compound.

Values of K_{12} and K_{13} were calculated from rate data on the respective binary systems, cyclohexane-cyclohexanol and cyclohexane-cyclohexanone. Expressions for calculating K_{12} and K_{13} are readily obtained by combining Equations (6) and (7), rearranging the resulting equation, and evaluating all quantities at zero time:

$$K_{12} = [(-dC_1/dt)_0/(R_1 - (-dC_1/dt)_0)] \times (C_2/C_1)_0 \quad \text{when } C_3 = 0 \qquad (15)$$

$$K_{13} = [(-dC_1/dt)_0/(R_1 - (-dC_1/dt)_0)] \times (C_3/C_1)_0 \quad \text{when } C_2 = 0 \qquad (16)$$

CONCLUSIONS

The radiolytic oxidation of cyclohexane in aqueous solution is sustained through the indirect action of radiation. In a radiation field, dissolved molecules of cyclohexane are attacked by free radicals produced by the radiolysis of water molecules. When dissolved oxygen gas is present, a number of oxidation products are formed including cyclohexanol, cyclohexanone, hydrogen peroxide, and trace quantities of carbon dioxide.

The experimental data were correlated well by using a simplified kinetic model which considers simultaneous reactions that occur between a single primary radical and competing reactive solutes that are present in the system. The model is in accord with the following generalizations regarding the kinetics of radiation-chemical reactions in dilute solution, which are supported by the experimental evidence obtained in this study:

1. The rate of reaction of a single reactive solute is independent of the concentration of that material. At a given radiation dose rate, the rate of reaction is a constant that is characteristic of the particular compound.

2. When more than one reactive solute is initially present or when a single solute is partially converted to a product, which undergoes further radical attack, the rate of disappearance of each solute will depend on the composition of the solution. In general, a plot of the concentration of each solute vs. time on cartesian coordinates will not be linear since the relative concentrations of the reactive solutes will change as the reaction proceeds.

3. The maximum attainable concentration of an intermediate product is determined by the relative values of the rate constants for all competing reactions. Providing diffusional limitations are absent, which could alter the course of the reaction at higher dose rates, the maximum concentration is independent of dose rate.

NOTATION

C_1 = concentration of cyclohexane, millimole/liter
C_2 = concentration of cyclohexanol, millimole/liter
C_3 = concentration of cyclohexanone, millimole/liter
C_4, C_5, C_6 = concentration of unidentified product, millimole/liter
f_{ij} = fraction of component i initially converted to product j
k_i = second-order rate constant, liters/(millimole-min.)
K_{1i} = dimensionless relative rate constant, k_1/k_i
$r\cdot$ = concentration of primary radical, millimole/liter
r_i = rate of disappearance of a specified solute in a solution containing other reactive solutes, millimole/(liter-min.)
R_i = rate of disappearance of pure solute in solution, millimole/(liter-min.)
R^* = rate of formation of primary radical, millimole/(liter-min.)
t = irradiation time, min.
α_i = proportionality constant in Equation (2)

Subscripts

0 = at zero time
i = ith component

LITERATURE CITED

1. Allen, A. O., "The Radiation Chemistry of Water and Aqueous Solutions," D. Van Nostrand Co., New York (1961).
2. Anonymous, *Chem. Week*, **93**, No. 20, 74 (1963).
3. Ashline, R. C., Ph.D. dissertation, Cornell Univ., Ithaca, N.Y. (1965).
4. Burns, W. G., R. Barker, B. A. Lewis, and E. J. York, *Trans. Faraday Soc.*, **61**, 2686 (1965).
5. Cates, H. L., Jr., J. O. Punderson, R. W. Wheatcroft, and A. B. Stiles, U. S. Patent No. 2,851,496 (1958).
6. Dyne, P. J., D. R. Smith, and J. A. Stone, *Ann. Rev. Phys. Chem.*, **14**, 313 (1963).
7. Engquist, E. H., and J. J. Martin, "Irradiation of Aqueous Solutions of Benzene to Produce Phenol", Presented at the 56*th* Annual Meeting, American Institute of Chemical Engineers, Houston, Texas, December 5, 1963.
8. Fricke, H., *Ann. N.Y. Acad. Sci.*, **59**, 567 (1955).
9. Ganguly, A. K., and J. L. Magee, *J. Chem. Phys.*, **25**, 129 (1956).
10. Irmann, F., *Chem. Ing. Tech.*, **37**, 793 (1965).
11. Johnson, G. R. A., and J. Weiss, *Chem. & Ind.*, **13**, 358 (1955).
12. Phung, P. V., and M. Burton, *Radiation Res.*, **7**, 199 (1957).
13. Proskurnin, M. A., and Y. M. Kolotyrkin, *Proc. U. N. Intern. Conf. Peaceful Uses At. Energy, 2nd, Geneva*, **29**, 52 (1958).
14. Schwarz, H. A., *J. Am. Chem. Soc.*, **77**, 4960 (1955).
15. Spielman, M., *AIChE J.*, **10**, 496 (1964).
16. Steeman, J. W. M., S. Kaarsemaker, and P. J. Hoftyzer, *Chem. Eng. Sci.*, **14**, 139 (1961).
17. Swallow, A. J., "Radiation Chemistry of Organic Compounds," Pergamon Press, New York (1960).
18. Teplý, J., and J. Bednář, *Proc. U.N. Intern. Conf. Peaceful Uses At. Energy, 2nd, Geneva*, **29**, 71 (1958).
19. Weiss, J., *Trans. Faraday Soc.*, **43**, 314 (1947).

Manuscript received September 1, 1967; revision received April 2, 1968; paper accepted April 5, 1968.