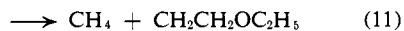
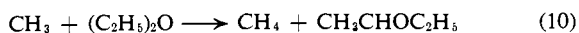
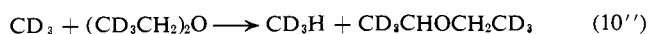
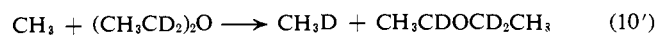


scavengeable hydrogen. This is consistent with the idea that the unscavengeable hydrogen is formed from very reactive species that react with less selectivity than do those which form the scavengeable hydrogen.

A rate constant ratio and isotope effect involved in methane formation can be calculated using results from the liquid phase radiolysis of ether (Table VI). For simplicity it will be assumed that methane was formed only by the reactions



If methane were formed by other reactions, the rate constant ratio and isotope effect reported here could readily be transferred to those reactions. Approximate values of  $k_{10}/k_{11}$  and  $k_{\text{H}}/k_{\text{D}}$  can be calculated as follows.



From the data in Table VII,  $k_{10'}/k_{11'} = 0.92$  and  $k_{10''}/k_{11''} = 13.0$  for the uninhibited reaction. If the crude assumption is made that the isotope effects in all of the reactions (10', 11', 10'', and 11'') are the same, then  $k_{10}/k_{11} = (0.92 \times 13)^{1/2} = 3.5$  and  $k_{\text{H}}/k_{\text{D}} = (13/0.92)^{1/2} = 3.8$ . The inhibited methane yield is

less than one-fifth of the uninhibited yield, so little error is introduced into the calculation of the kinetic parameters by using the total methane yields in calculating the values for the scavengeable reactions.

Similarly,  $k_{10}/k_{11} = 2.5$  and  $k_{\text{H}}/k_{\text{D}} = 2.9$  for the unscavengeable reactions. As expected,  $k_{10}/k_{11}$  and  $k_{\text{H}}/k_{\text{D}}$  are smaller for the unscavengeable than for the scavengeable methane-forming reactions because the more reactive species that form the unscavengeable methane react with less selectivity than do those which form the scavengeable methane. The above values of  $k_{10}/k_{11}$  and  $k_{\text{H}}/k_{\text{D}}$  are probably too small because of the considerable amount of isotopic scrambling in the ether- $\beta$ - $d_6$  (see Table I).

In the radiolysis of liquid ether- $\alpha$ - $d_4$ , 72% of the ethylene formed was  $\text{C}_2\text{H}_2\text{D}_2$  (Table VII), which suggests that ethylene formation mostly involves  $\beta$ -C-H cleavage. The 28% of  $\text{C}_2\text{H}_3\text{D}$  indicates that  $\alpha$ -C-H cleavage also contributes to ethylene formation.

The ethylenes from ether- $\beta$ - $d_6$  confirm that both  $\beta$ - and  $\alpha$ -C-H cleavage occur, with a preference for  $\beta$ -cleavage. The larger apparent amount of isotopic scrambling in the ethylene from ether- $\beta$ - $d_6$  than in that from ether- $\alpha$ - $d_4$  is probably due to the larger amount of isotopic impurity in the ether- $\beta$ - $d_6$ .

It seems surprising that the ethylene compositions are so similar in the liquid and gas phase systems, in spite of the very different ethylene yields in the two phases.

The presence of 1,3-pentadiene had little effect on the isotopic distribution of the ethylenes.

## Energy Transfer and Radical Scavenging in the Radiolysis of Solutions of *p*-Benzoquinone in Cyclohexane

F. C. Goodspeed and J. G. Burr

Contribution from the North American Aviation Science Center, Thousand Oaks, California. Received December 7, 1964

$\gamma$ -Radiolysis of 40 mM benzoquinone in cyclohexane solutions gives the following products (the numbers are yields in molecules/100 e.v. absorbed in the whole solution): cyclohexene, 1.0; bicyclohexyl, 0.15; hydrogen, 3.1; monocyclohexylquinone, 4.4; hydroquinone (mostly as the quinhydrone), 3.1. Quinone is consumed with a *G* value of 10.8; quinone-containing products are formed with a *G* value of 10.6. Photolysis of saturated quinone solutions (40 mM) gives cyclohexylquinone and hydroquinone (as the quinhydrone); no cyclohexene or bicyclohexyl could be detected. The quinone recovered from a  $\gamma$ -irradiated solution of quinone in tritiated cyclohexane did not contain any radioactivity, indicating that quinone does not scavenge hydrogen atoms in this system under these conditions. These data are interpreted in terms of a set of processes which includes the scavenging of cyclohexyl radicals with a yield of 3.4 molecules/100 e.v. absorbed, deactivation of activated cyclohexane molecules by quinone with a yield of 2.3 (followed by reaction of about 50% of the activated

quinone molecules with cyclohexane), and a "molecular" process for cyclohexene and hydrogen with a yield of 1.0.

### Introduction

The presence of dissolved benzene, cyclohexene, or quinone in irradiated cyclohexane alters the yields of hydrogen, bicyclohexyl, and cyclohexene from the cyclohexane and results in the formation of new products. The nature of the interaction producing these changes depends upon the nature of the solute. In the case of benzene the interaction has been shown<sup>1</sup> to be partly one of radical scavenging and partly one of energy transfer; the interaction of cyclohexene during the radiolysis can be described almost entirely in terms of radical scavenging.<sup>2</sup> The purpose of this investiga-

(1) J. G. Burr, J. D. Strong, and F. C. Goodspeed, *J. Chem. Phys.*, **40**, 1433 (1964).

(2) M. Cher, C. Hollingsworth, and B. Browning, *ibid.*, **41**, 2270 (1964).

tion was to determine the mode of quinone interaction. We have accomplished this by a complete determination of the nature and yields of all products formed in the radiolysis of cyclohexane-quinone solutions, by comparing these yields with the yields of products from pure cyclohexane, by an isotopic tracer experiment, and by comparison to the photochemistry of these solutions.

A similar investigation was carried out by Waight and Walker several years ago<sup>3</sup>; we have improved the analytical techniques used to measure the yields of several of the radiolysis products and extended the number and variety of measurements; our interpretation is different.

## Experimental

**Materials.** The cyclohexane used was Eastman spectroscopic grade. It contained a total of about 1.0% other saturated hydrocarbons, which showed up as three small peaks ahead of the cyclohexane on a propionitrile-silver nitrate column, but no olefinic impurities. The benzoquinone was Eastman practical grade, sublimed twice, m.p. 114°; the quinhydrone was Baker and Adamson reagent, not further purified.

**Preparation and Irradiation of Samples.** Hydrogen and hydroquinone yields were usually determined by irradiating 5-ml. solutions of appropriate concentration in ampoules with break-off tips, degassed by conventional freeze-melt techniques. Samples were occasionally irradiated in Pyrex vessels of either 50- or 150-ml. capacity, equipped with a central fritted tube for bubbling of inert gas and a closable outlet. Bicyclohexyl and cyclohexylquinone yields were determined from solutions contained in 25-ml. evacuated, sealed ampoules. The solutions were deaerated by bubbling with argon for 1 hr. Concentrations were corrected for loss of solvent during degassing.

**Analysis of Products.** A. Hydrogen was determined by freezing out all components at -196° and measuring the residual gas on a Toepler pump gas buret. Mass spectrometric analyses of two of the samples showed 99+ % H<sub>2</sub>.

B. Quinhydrone was determined by centrifugation of the irradiated solutions and weighing the precipitate. *Anal.* Calcd. for quinhydrone: C, 66.54; H, 5.20; O, 28.06. Found for 10% cyclohexyl substitution of the quinone: C, 67.07; H, 4.88; O, 28.10. This value of 10% was used as the amount of cyclohexylquinone. Attempts to determine the amount of substituted quinone by g.l.c. gave irreproducible values but indicated a somewhat higher amount of substitution.

C. Quinone concentrations were measured by g.l.c. on a 10% DC704 silicon oil on Fluoropak column, 0.25 in. × 6 ft. Column temperature was 120°; flow rate of helium was approximately 60 cc./min. Peak areas were obtained with a disk integrator and the results standardized against quinone solutions of known concentration.

D. Cyclohexylquinone was identified by ultraviolet, infrared, and n.m.r. spectra. It was not possible to obtain a large enough pure sample to get a good melting point. The original sample was evaporated to dryness, then redissolved in CS<sub>2</sub>. The concentration of cyclo-

hexylquinone was estimated from the intensity of the 2028-cm.<sup>-1</sup> C-H band in the infrared region. The band intensity was calibrated using an authentic sample of cyclohexylquinone obtained from M. Reintjes, University of California at Riverside. The results so obtained were corrected (by small amounts) for the presence of bicyclohexyl in the residue (estimated as above by g.l.c.) and for the coprecipitation of cyclohexylquinone in quinhydrone.

E. Total hydroquinones were determined from the absorbance at 2950 Å., in ether, using the absorption coefficient determined for pure hydroquinone. The assumption was made that if any substituted hydroquinone was present, the absorption coefficient would not change very much. Substituted hydroquinones are oxidized by benzoquinone to yield the substituted quinone and hydroquinone. (See discussion in footnote 6.)

F. Bicyclohexyl was determined by g.l.c. on a 2-ml. solution concentrated from a 25-ml. sample, using a solution of known bicyclohexyl concentration as the standard.<sup>1,2</sup>

**Photolysis of Benzoquinone-Cyclohexane Solutions.** A 40-ml. solution of 4.0 mg./ml. of benzoquinone in cyclohexane was deaerated with argon for 1 hr. in a volumetric flask and photolyzed for 2 hr. with an ME/D 250-w. medium pressure lamp. The quinhydrone precipitate weighed 32.2 mg. No cyclohexene was detectable by g.l.c. under the same condition in which a solution 0.0311 mg./ml. of cyclohexene in cyclohexane gave a barely detectable peak. This lower detection limit corresponded to about 1.2 mg. of total cyclohexene formed, establishing the yield of cyclohexene as at most about 4% of the quinhydrone formed. This compares to about 30% in the radiolysis of solutions of the same composition. No bicyclohexyl was detected in a 5-ml. solution saturated with benzoquinone, photolyzed, and then concentrated to approximately a 1-ml. volume (in this photolysis 41.6 mg. of quinhydrone was formed). The sensitivity of the chromatograph makes it possible to say that the bicyclohexyl yield must be less than 10% of the quinhydrone yield. The quantum yield was estimated to be about 0.5, using UO<sub>2</sub>C<sub>2</sub>O<sub>4</sub> actinometry.

**Radiolysis of Solutions of Quinone in Tritiated Cyclohexane.** A solution of 3.61 mg./ml. of quinone in tritiated cyclohexane (6.77 × 10<sup>6</sup> c.p.m./50-λ solution) was prepared by weight. One-ml. samples of this solution, degassed by the freeze-melt technique, were given a dose of 0.9 × 10<sup>20</sup> e.v./g. of cobalt-60 γ-rays. Two-hundred-microliter samples of the irradiated solutions were fractionated by gas chromatography on a 3/8 in. × 6 ft. silicon oil 704 on firebrick column at 120°. The quinone fraction was collected in Hamilton collector U-tubes (indented, like a Vigreux distillation column) chilled with liquid nitrogen. The collected quinone was rinsed out of the U-tubes with a weighed amount of inactive cyclohexane, and this solution was rechromatographed. Prior to this rechromatographing, the column was rinsed by passage of numerous samples of inactive cyclohexane and passage of helium flow overnight until the quinone fraction collected from a test solution reached a constant activity (usually this was still several times the background count as determined by sample counting of a

(3) E. S. Waight and P. Walker, *J. Chem. Soc.*, 2225 (1960).

quinone solution). The quinone fraction collected from the rechromatographing was removed from the U-tube with a weighed amount of cyclohexane. The quinone content of this solution was determined by analytical chromatography in a Loenco instrument, and the radioactivity of the quinone determined by counting 100- and 200- $\lambda$  samples of the solution. The specific activity of the quinone thus obtained was found to be the same as that of a quinone sample obtained by an identical procedure from an unirradiated solution of quinone in tritiated cyclohexane and that obtained from a solution of quinone in inactive cyclohexane obtained from a thoroughly rinsed column. This final activity for 100- $\lambda$  samples of the three quinone solutions (all containing about the same quinone concentration) was about 270–279 c.p.m./100  $\lambda$ .

## Results and Discussion

The data which we have obtained are shown in Table I. The variations in quinhydrone and hydrogen yields with quinone concentration are also displayed in

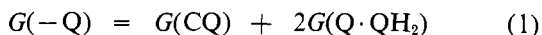
Table I. Product Yields

Product	No. of runs	Dose $\times 10^{-19}$ , e.v./ml.	[Q] $\times 10^3$ , M	Yield <sup>a</sup>
H <sub>2</sub>	.. <sup>b</sup>	8.32	40.41	3.08
QH <sub>2</sub>	3	9.23	37.01	3.10 $\pm$ 0.2
(C <sub>6</sub> H <sub>11</sub> ) <sub>2</sub>	1	7.58	36.87	0.14 $\pm$ 0.05
C <sub>6</sub> H <sub>10</sub>	3	8.71	37.46	1.05 $\pm$ 0.05
CQ	8	(7.5) <sup>c</sup>	(37.5) <sup>c</sup>	4.4 $\pm$ 0.2
(Q·QH <sub>2</sub> )	.. <sup>b</sup>	(7.8) <sup>c</sup>	(37.2) <sup>c</sup>	3.03
-Q	5	(7) <sup>c</sup>	(37) <sup>c</sup>	10.9 $\pm$ 0.5

<sup>a</sup> Molecules/100 e.v. absorbed. <sup>b</sup> See Figure 1. <sup>c</sup> Average values.

Figure 1; it is evident that the changes in product yield have nearly reached a plateau at the saturation quinone concentration of about 40 mM. Our values are in general agreement with those already reported in the literature.<sup>4</sup>

These results can be checked initially and most simply in terms of a set of material balances. A good hydrogen balance has been observed in the radiolysis of pure cyclohexane.<sup>1,4</sup> For the 40 mM quinone solutions, several material balances can be written. The first of these is a material balance for quinone consumed and quinone appearing in the radiolysis products; this is shown in eq. 1, where CQ is cyclohexylquinone, Q is quinone, and QH<sub>2</sub> is hydroquinone.



The value of the left-hand side is 10.8 (Table I) and that of the right-hand side is 4.4 + 6.2 or 10.6. The good agreement in this balance shows that we have accounted satisfactorily for all quinone-containing products.

Another material balance in the quinone solutions is again the hydrogen balance. This balance can be obtained simply by equaling the yields of products

(4) (a) S. K. Ho and G. R. Freeman, *J. Phys. Chem.*, **68**, 2189 (1964); (b) P. J. Dyne and J. A. Stone, *Can. J. Chem.*, **39**, 2381 (1961).

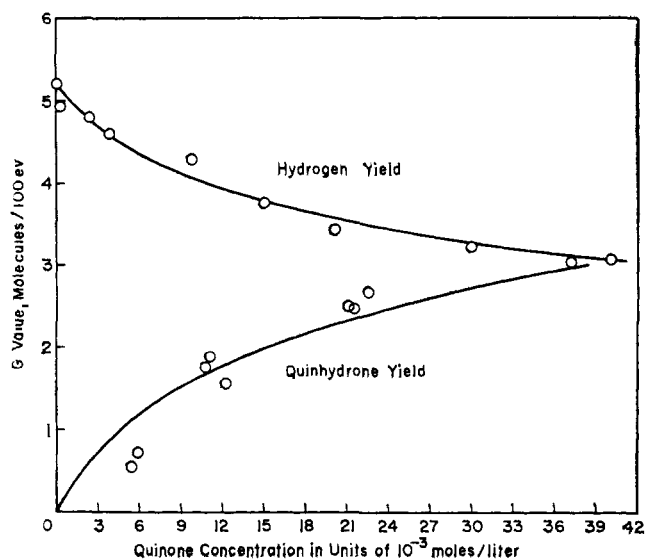
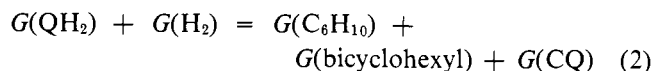


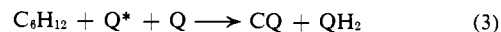
Figure 1.

showing a hydrogen deficit to those containing product hydrogen. It is shown in the following equation.



The sum of the values in the left-hand side is 6.2, and the sum for the right-hand side is 5.6. This is a little less satisfactory material balance than the hydrogen balance for the products from pure cyclohexane,<sup>1,4</sup> but it is almost within the error limits of the summed analyses, and this, taken together with the excellent material balance for quinone and the consequent improbability that there are substantial amounts of undiscovered products, seems good grounds for believing that the agreement between hydrogen-containing products and hydrogen-deficient products is good.

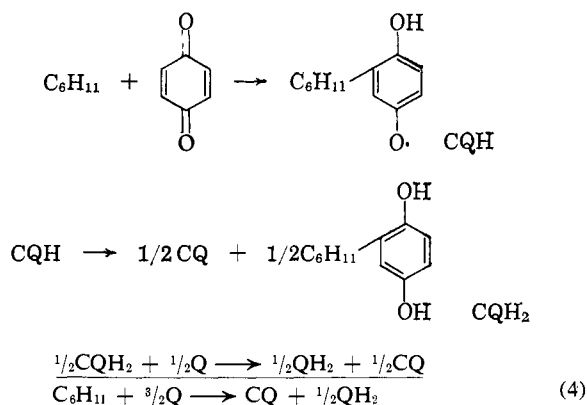
The new products which appear in the quinone solution are cyclohexylquinone and hydroquinone (as quinhydrone). These products can be formed by scavenging of hydrogen atoms or cyclohexyl radicals or by reaction of an excited quinone molecule with cyclohexane. The reality of the latter process is demonstrated by the photochemical experiments described here and also by other reports about the light-induced reactions of quinone molecules with saturated organic molecules such as carbinols.<sup>5</sup> The products of the photochemical process are cyclohexylquinone and hydroquinone in equimolar amounts



Scavenging of hydrogen atoms and/or cyclohexyl radicals may be occurring also. The scavenging of cyclohexyl radicals by quinone can result in the formation of both cyclohexylquinone and hydroquinone, according to reaction 4.<sup>6</sup> It should be noted that

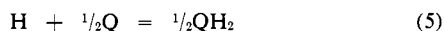
(5) (a) L. Paoloni and G. B. Marini-Bettolo, *Gazz. chim. ital.*, **87**, 395 (1957); (b) B. Atkinson and M. Di, *Trans. Faraday Soc.*, **54**, 1331 (1958).

(6) The mechanisms for the substitution of quinones by free radicals do not appear to be as well known as they should. However, the processes summed up in (4) are reactions which seem to be widely accepted: J. Cason "Organic Reactions," Vol. IV, John Wiley and Sons, Inc., New York, N. Y., 1948, pp. 321, 322; E. H. Rodd, "Chemistry of Carbon Compounds," Vol. IIIB, Elsevier Publishing Co., New York, N. Y., 1956, pp. 693, 698; C. Walling, "Free Radicals in Solution," John Wiley and Sons, Inc., New York, N. Y., 1957, p. 166 ff.

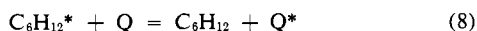
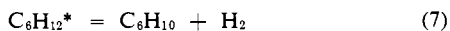
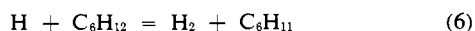


hydroquinone is a product of cyclohexyl radical scavenging. Since hydroquinone is formed in eq. 3-5, its formation does not necessarily demonstrate quinone scavenging of hydrogen atoms.

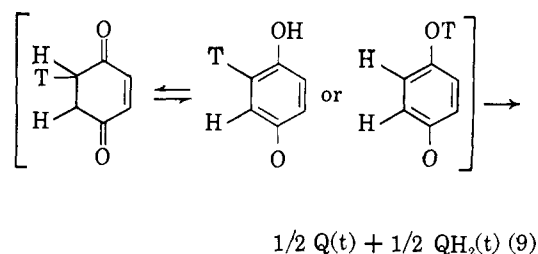
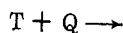
A preliminary guide to the reactions occurring in radiolysis of the quinone solutions may be obtained by considering the relative amounts of cyclohexylquinone and hydroquinone. These yields can be considered to reflect the relative contributions of the reactions 3-5. If the two products are simply the result of hydrogen atom scavenging (5) and cyclohexyl radical



scavenging (4) and if, for the moment, interaction between CQH and QH is neglected, then  $G(\text{QH}_2) = \frac{1}{2}G_5 + \frac{1}{2}G_4$ . Since  $G(\text{CQ}) = G_4 = 4.4$ ,  $G_5$  must equal 1.8. This deduction is, however, inconsistent with the observed yield of cyclohexylquinone. The inconsistency follows from the following reasoning:  $G(\text{H}_2) = G_6 + G_7$  and  $G(\text{H}) = G_5 + G_8$ ; when  $G(\text{H}_2) = 3.1$ ,  $G_7 = 1.0$  (equal to  $G(\text{C}_6\text{H}_{10})$ ), and  $G_5 = 1.8$ , then  $G(\text{H}) = 3.9$ . If  $G(\text{H}) = 3.9$  and  $G(\text{C}_6\text{H}_{11}) = G(\text{H}) + G_6$ , then  $G(\text{C}_6\text{H}_{11})$  would have to be 6.0—but the observed value is that derived from  $G(\text{CQ})$ , or 4.4. Thus, the assumption of pure radical scavenging leads to stoichiometrical difficulties. Obviously, energy-transfer processes, such as by reaction 8, cannot be neglected.

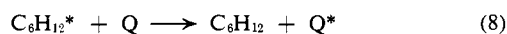
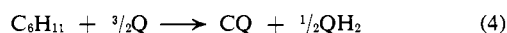
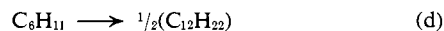
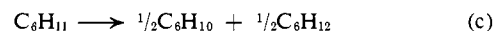
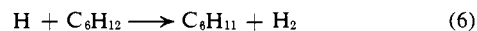
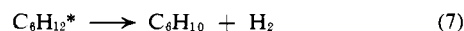
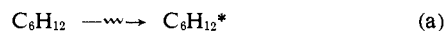


The tritium tracer experiments are a strong indication that the yield of the hydrogen atom scavenging process (5) is actually zero. The absence of any tritium activity in the quinone isolated from the irradiated solutions of quinone in tritiated cyclohexane means that the labeled hydrogen atoms, at all events, have not added to the quinone ring system since the result of this would be inevitably the retention of some tritium in the quinone ring system as a result of radical disproportionation reactions. Other radicals react with the quinone ring by displacement-rearrangement type of processes such as are summed up in (4). Since there is a dynamic equilibrium among the keto-enol tautomers shown in eq. 9, addition of the labeled hydrogen atoms either to ring or to oxygen would result in the retention of radioactivity in the recovered quinone; this is not observed. The combination of this tracer evidence together with the stoichiometrical difficulties shown above leads to the conclusion that, in this system at



least, quinone does not scavenge any hydrogen atoms by an addition process.

A more productive assumption is that the two products are the result of the photochemical process (3) plus cyclohexyl radical scavenging (4). Using algebra similar to that above, the appropriate yields of the two processes are  $G_4 = 2.6$  and  $G_3 = 1.8$ . The decrease in  $G(\text{H}_2)$  between pure cyclohexane and the quinone solution must then be explained by an energy-transfer process (8), whose yield is  $G_8 = 5.4 - 3.1 = 2.3$ . A large fraction of the excited quinone molecules ( $\text{Q}^*$ ),  $G_3/G_8 = 0.8$ , then reacts with cyclohexane according to reaction 3. More accurate values for these yields can be obtained by considering the more complete set of processes shown in the equations



The yields of these processes can be related by a set of conservation equations

$$G_7 + G_6 = 3.1 \quad (\text{A})$$

$$G_b = G_6 \quad (\text{B})$$

$$G_d = 2G(\text{C}_{12}\text{H}_{22}) = 0.3 \quad (\text{C})$$

$$G_4 = G_b + G_6 - G_c - G_d \quad (\text{D})$$

$$G_8 = 5.4 - G_7 - G_b \quad (\text{E})$$

$$G_3 = G(\text{CQ}) - G_4 \quad (\text{F})$$

$$G_3 = G(\text{QH}_2) - \frac{1}{2}G_4 \quad (\text{G})$$

and two empirical relationships, H and I. Relationship H reflects the observation that the "unscavengeable"

$$G_7 = 0.5G_6 \quad (\text{H})$$

$$G_c = 1.3G_d \quad (\text{I})$$

yields of cyclohexene and hydrogen in the radiolysis of pure cyclohexane appear to be about one-third of the total hydrogen<sup>1,4</sup> together with the assumption that the presence of quinone will not affect the relative probability of reactions 7 and b; the results are not very sensitive to the value assumed for  $G_7/G_b$ . The other relationship, I, is taken from the known disproportionation/

recombination ratio for cyclohexyl radicals, which is 1.3.<sup>7</sup> There are more equations (A–I) than unknowns, and the set is easily solved; the redundancy supplies a check for internal consistency. The important yield values are

$$\begin{aligned} G_7 \equiv G_m(\text{H}_2) \equiv G_m(\text{C}_6\text{H}_{10}) &= 1.0 & G_8 &= 2.3 \\ G_b = G(\text{H}) &= 2.1 & G_3 &= 1.0\text{--}1.4 \\ G_4 &= 3.4 \end{aligned}$$

The two values of  $G_3$  come from (F) and (G), and the agreement reflects the amount of internal consistency in the calculations. The values of these yields are in reasonable accord with those to be expected from the literature and from comparison with other experiments.  $G_7$  is the "molecular" yield of hydrogen or cyclohexene; our value of 1.0 is lower than that observed by Cher for cyclohexene–cyclohexane solutions<sup>2</sup> (where the solute is acting solely as a radical scavenger, and little energy transfer occurs) of 1.66. A lowering of the molecular yield would be expected since the value of  $G_8 = 2.3$  shows that a considerable amount of energy transfer must be taking place. In fact, if the value of  $G_a$  is taken to be 5.4, then the value of  $G_7$  should be  $(3.1/5.4) \times 1.66 = 0.96$ , which is in excellent agreement with the experiment. The value of  $G(\text{H})$  in the quinone solution is similarly calculated to be 2.1, which compares equally well with  $G_b = 2.1$ .

The value of 2.3 for  $G_8$ , the energy-transfer reaction, is also obtained from  $\Delta G(\text{H}_2)$ , which is  $5.4 - 3.1 = 2.3$ . The relative values of  $G_8$  and  $G_3$  give the fraction of quinone molecules which accept energy from cyclohexane and then immediately react with cyclohexane according to (3). This fraction is about 1.3/2.3, or

(7) C. E. Klots and R. H. Johnsen, *Can. J. Chem.*, **41**, 2702 (1963).

about 0.5; this can be compared with the quantum yield of 0.5 observed for the photochemical reaction (3) although this is not to say that the quinone is necessarily in the same excited state in each case.

We feel that this combination of complete product determination, with the stoichiometric analyses, the tracer experiments, and the demonstration of a pertinent photochemical process, has enabled a firm and complete description of the principal reaction paths in the radiolysis of cyclohexane solutions of quinone. It is evident that both radical scavenging and energy transfer are taking place and that nearly one-half of the excited cyclohexane molecules which would normally dissociate are deactivated by the quinone. One of the most striking features of the analysis is the conclusion that hydrogen atoms are not scavenged by the quinone. The possibility can be considered that (6) is fast enough to consume all the H atoms before they encounter a quinone molecule, as follows. The collision frequency in liquid is about  $10^{13}$  sec.<sup>-1</sup>, and the abundance of quinone molecules in 40 mM solutions is 1/250, so that the collision efficiency of H atoms with  $\text{C}_6\text{H}_{12}$  would have to be better than 1/250 for them all to react with cyclohexane before an encounter with a quinone molecule. The reported<sup>8</sup> collision yield (in gas phase) for the reaction of hydrogen atoms with cyclohexane is much less than this, about  $10^{-7}$  at room temperature. Reaction 6 hardly seems fast enough to explain the facts, and explanation must reside in some peculiarity of the quinone–hydrogen atom interaction.

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(8) A. F. Trotman-Dickenson, "Gas Kinetics," Butterworth and Co. Ltd., London, 1955, p. 177.

## A Photoisomerization Reaction of Cyclic Ketones in the Liquid Phase<sup>1</sup>

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It has been found that six-, seven-, and eight-membered cyclic ketones, when irradiated as pure liquids with light of 3130 Å., undergo a ring contraction reaction to give the 2-methyl derivative of the cyclic ketone with one less carbon. The reaction accounts for 6% of the cyclohexanone that undergoes photolysis but only 0.2% in cycloheptanone. A variant of this reaction gives 2-n-propylcyclopentanone in the photolysis of cyclooctanone. In cyclohexanone the reaction has a quantum yield of 0.03. This value decreases in solutions of cyclohexanone in cyclohexane. At a given concentration, the addition of cyclohexene has no effect on the yield. Substitution of the ring by a methyl group in the 2-position seems to

obscure the reaction, while in the 3-position only one of the two possible dimethylcyclopentanones is formed. In the photolysis of cyclohexanone-2,2,6,6-d<sub>4</sub>, the product corresponded to  $\overline{\text{COCH}(\text{CHD}_2)\text{CH}_2\text{CH}_2\text{CD}_2}$ . The reaction is believed to involve the transfer of a proton from the 3- to the 2-position in a configuration in which the ring is substantially intact.

### Introduction

Although the photochemical reactions of cyclic ketones in the condensed phase were first studied 50 years ago,<sup>2,3</sup> there has been no systematic study up to

(1) For a preliminary communication, see S. E. Cremer and R. Srinivasan, *J. Am. Chem. Soc.*, **86**, 4197 (1964).

(2) G. Ciamician and P. Silver, *Chem. Ber.*, **41**, 1071 (1908).

(3) G. Ciamician and P. Silver, *ibid.*, **42**, 1510 (1909); **46**, 3077 (1913).