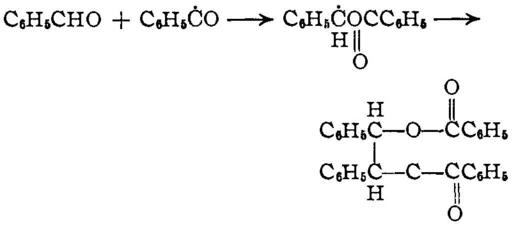
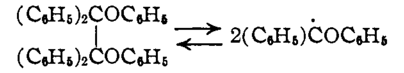


(15)

reaction 16. In this connection, also, it may be noted that oxygen reacts readily with $(C_6H_5)_2C(CH_3)C(CH_3)(C_6H_5)_2$, presumably, because this ethane dissociates into free radicals.[24]



$$(C_6H_5)_2COC_6H_5{-}(C_6H_5)_2COC_6H_5 \rightleftarrows 2(C_6H_5)\dot{C}OC_6H_5 \qquad (16)$$

Reaction 14 merely represents the dissociation of a hemiketal and would provide an alternate route to benzopinacol from II.

Mechanism of Photoöxidation in the Presence of Benzophenone.—It is evident from the results in Table II that the acetone yield is independent of the oxygen concentration in the system but the yield of benzopinacol is reduced from about unity in an oxygen free system to zero when the solution is saturated with oxygen and irradiated. In the latter case significant yields of hydrogen peroxide are also obtained, but the benzophenone in the system apparently is not used up in the reaction. Apparently the $(C_6H_5)_2\dot{C}OH$ radicals are being destroyed by the oxygen, and the following mechaism seems to afford a reasonable explanation

$$(C_6H_5)_2CO + h\nu \longrightarrow (C_6H_5)_2CO^* \qquad (1)$$

$$(C_6H_5)_2CO^* + CH_3CHOHCH_3 \longrightarrow (C_6H_5)_2\dot{C}OH + CH_3\dot{C}(OH)CH_3 \qquad (2)$$

$$(C_6H_5)_2\dot{C}OH + O_2 \longrightarrow HO_2 + (C_6H_5)_2CO \qquad (17)$$

$$CH_3\dot{C}(OH)CH_3 + O_2 \longrightarrow H\dot{O}_2 + CH_3COCH_3 \qquad (18)$$

$$H\dot{O}_2 + CH_3\dot{C}(OH)CH_3 \longrightarrow H_2O_2 + CH_3COCH_3 \qquad (19)$$

$$H\dot{O}_2 + (C_6H_5)_2\dot{C}OH \longrightarrow H_2O_2 + (C_6H_5)_2CO \qquad (20)$$

This phase of the problem was not studied in detail; hence it seems appropriate simply to point out that this mechanism is merely one sequence of reactions compatible with an over-all quantum yield of unity for acetone, zero for benzopinacol and an intermediate value for hydrogen peroxide. Qualitatively these products agree with those found by Bäckström for irradiation of a benzophenone-isopropyl alcohol oxygen system at 3660 Å. However, he reports almost quantitative yields of both acetone and hydrogen peroxide.[25]

In the present research, no attempt was made to achieve quantitative yields of the peroxide so that the differences in reported ratios of peroxide and ketone may be only an apparent anomaly. Furthermore, it is clear from the qualitative agreement between Bäckström and these authors that the reports of earlier investigators of photoöxidations,[20,26] in this system, one of whom reported a chain length of 18 for the oxidation[26] and water as a product (but no H_2O_2), warrant critical examination.

Acknowledgments.—The authors acknowledge with thanks helpful discussions with Messrs. E. R. Bell, J. Calvert, J. Garst and H. Johnson.

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[24] K. Ziegler, R. B. Whitney and P. Herte, *Ann.*, **551**, 187 (1942).

[25] H. Bäckström, "The Svedberg" (Memorial Volume), 1944, p. 45.

[26] A. Berthoud, *Helv. Chim. Acta*, **16**, 592 (1933).

RIVERSIDE, CALIF.

[CONTRIBUTION FROM THE LABORATORY OF TECHNICAL DEVELOPMENT, NATIONAL HEART INSTITUTE]

Formation of Hydrogen Peroxide by Ultrasonic Waves: Free Radicals

BY ALFRED WEISSLER

RECEIVED JULY 17, 1958

In order to study the role of free radicals in chemical reactions caused by ultrasonic waves, the ultrasonic yield of hydrogen peroxide has been measured in water which contained radical scavengers in various concentrations and also was saturated with either oxygen or argon. The scavengers used were acrylamide, formic acid and allylthiourea. The results provide evidence that OH radical is an intermediate in the sonochemical production of H_2O_2. Further, it was observed that a radical scavenger may be efficient even though relatively unvolatile and therefore present in low concentration inside the cavitation bubble. Some differences between sonochemistry and radiation chemistry are pointed out, particularly that the destruction of hydrogen peroxide by back reaction with H or OH radicals is less important than in radiation chemistry. The experiments were carried out by treating 50 ml. of liquid in a 32 × 200 mm. Pyrex cell with 20 watts of acoustic energy at a frequency of 400 kilocycles/sec.

Introduction

Attempts to understand the mechanism by which intense ultrasonic waves cause chemical changes in liquid systems[1-9] have led to a variety of hypotheses. One of these, which has recently attracted much support,[10-14] attributes the sono-

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[1] A. Weissler, H. W. Cooper and S. Snyder, THIS JOURNAL, **72**, 1769 (1950).

[2] A. V. M. Parke and D. Taylor, *J. Chem. Soc.*, 4442 (1956).

[3] A. I. Virtanen and N. Ellfolk, *Acta Chem. Scand.*, **4**, 93 (1950).

[4] A. Weissler, *J. Acous. Soc. Am.*, **25**, 651 (1953).

[5] I. E. El'piner and A. V. Sokol'skaya, *Biofizika*, **2**, 225 (1957).

[6] V. Bellavita, F. A. Levi and N. Cagnoli, *Ann. Chim. (Rome)*, **45**, 248 (1955).

[7] A. Weissler, *J. Appl. Phys.*, **21**, 171 (1950).

[8] A. Henglein, *Z. Naturforsch.*, **10b**, 20 (1955); *Makromol. Chem.*, **14**, 15 (1954).

[9] R. O. Prudhomme, D. Picard and R. G. Busnel, *J. chim. phys.*, **50**, 107 (1953).

[10] O. Lindstrom, *J. Acous. Soc. Am.*, **27**, 654 (1955).

[11] P. Alexander and M. Fox, *J. Polymer Sci.*, **12**, 533 (1954).

[12] R. O. Prudhomme, *J. chim. phys.*, **54**, 332 (1957).

[13] M. A. Khenokh and E. M. Lapinskaya, *Zhur. Obschchei Khim.*, **26**, 2439 (1956).

[14] E. C. Steiner and J. Karpovich, paper K8 presented at the October 1957 meeting of the Acoustical Society of America, Ann Arbor, Michigan.

chemical reactions to free radical intermediates (H, OH, perhaps also HO_2 and others) formed during the cavitation process. The radicals are thought to be produced either by electrical discharges through the water vapor in the cavities[15–18] or by thermal dissociation due to adiabatic compression of the collapsing bubbles.[19]

It is apparent that there is a certain analogy between sonochemistry and radiation chemistry. Experimentally, this is closer for α-particle than X-ray effects,[20] a possible rationale being that both the α-track and the collapsing cavity are regions where the ionization and excitation energy are highly concentrated, in contrast to the linearly extended ionization path of X-rays.

In order to learn more about the extent of this analogy and also to obtain further information on free radical intermediates, the present work was undertaken. It is a study of a fundamental reaction brought about by ultrasound—the production of hydrogen peroxide in distilled water saturated with either oxygen or argon—from the standpoint of the changes in peroxide yield caused by efficient radical scavengers such as acrylamide,[21] formic acid[22] and allylthiourea[23] at various concentrations.

Experimental Details

The source of ultrasound employed was a Brush Hypersonic Generator with focusing barium titanate transducer model BU-301, operating at 400 kilocycles with a rated output of 250 electrical watts. Pyrex 32 × 200 mm. test-tubes, selected for uniformity of sonochemical yield, were used as reaction vessels, closed by a rubber stopper carrying inlet and outlet tubes for gassing. Reproducibility of positioning was obtained by lowering the test-tube into the transformer oil of the transducer assembly until it rested on the transducer, and then clamping it.

In a typical run, 50 ml. of distilled water (or a solution of the radical scavenger) were pipetted into the test-tube and saturated at 0° with oxygen (or argon) by bubbling the gas through at the rate of one liter per minute for 10 minutes, with frequent shaking. As soon as the gassing was completed, both the inlet and outlet tubes were closed off securely, to eliminate the possibility of access of air during the ensuing 10-minute treatment with ultrasound. (Preliminary experiments showed that the yield increased more or less linearly with duration of treatment, up to and beyond 10 minutes.) The generator was operated at 170 ma. cathode current, which corresponded to about 20 acoustic watts inside the reaction vessel, or 2.5 watts/sq. cm., as measured by both calorimetry and radiation pressure. Cooling water was circulated rapidly through the transducer assembly, in order to reduce the heating effect; even so, the temperature of the reaction mixture rose as high as 40° by the end of the run, after which it was cooled to 20° by brief immersion in ice-water.

The sonochemical yield of hydrogen peroxide was determined spectrophotometrically, using the yellow color of the titanium complex.[24] A 45-ml. aliquot of the irradiated solution was added to 5.0 ml. of standard titanium sulfate solution (prepared by dissolving 2.0 g. of "purified" Ti metal in 500 ml. of 1:4 H_2SO_4, oxidizing dropwise at 100° with HNO_3, boiling to expel nitrogen oxides and diluting to one liter) in a 50-ml. volumetric flask. After thorough mixing, the optical density was read on a Beckman spectrophotometer at 4100 Å. in a 50 mm. cell, against a blank of distilled water. (In case of turbidity or extraneous color, the H_2O_2 concentration was determined by differential measurement before and after destruction of the peroxide with a few milligrams of sodium sulfite.) By using known amounts of H_2O_2, it was found that under these conditions an optical density of 0.100 was equivalent to 0.0465 mg. of H_2O_2. Duplicate and frequently triplicate runs were made, the reproducibility being about 10% in accordance with the experience of other investigators.

High purity argon (99.9%) and oxygen (99.5%) were used; mass spectrometer analysis of the former showed less than 0.01% of either nitrogen or oxygen. The allylthiourea, 98+% formic acid and acrylamide were Eastman white label quality, the acrylamide being further purified before use by recrystallization from benzene–chloroform.

Results

The results obtained are shown in Figs. 1–3. In general, the observed yield of hydrogen peroxide decreased as the concentration of scavenger increased. Also, the yields were higher in oxygen-saturated than in argon-saturated solution. Further details, as well as the significance of the results, are discussed in the following section.

Discussion

Extensive studies have shown that the formation of hydrogen peroxide from water in radiation chemistry is a complex process, involving many interrelated reactions. A simplified description starts, in the ionization tracks, with the decomposition of water into hydrogen and hydroxyl free radicals.

$$H_2O \longrightarrow H + OH \qquad (1)$$

The radicals may recombine in unlike pairs to regenerate water, or in like pairs, to produce molecular hydrogen and hydrogen peroxide

$$H + H \longrightarrow H_2 \qquad (2)$$

$$OH + OH \longrightarrow H_2O_2 \qquad (3)$$

Also, some of the radicals may remain free long enough to react with added solute (radical scavenger, "Rs")

$$Rs + OH \longrightarrow RsOH \qquad (4)$$

or with the hydrogen peroxide and hydrogen produced as above destroying them by a chain reaction

$$H + H_2O_2 \longrightarrow H_2O + OH \qquad (5)$$

$$OH + H_2 \longrightarrow H_2O + H \qquad (6)$$

In oxygenated solutions, additional hydrogen peroxide may be formed by a route involving perhydroxyl (HO_2) radical

$$H + O_2 \longrightarrow HO_2 \qquad (7)$$

$$HO_2 + HO_2 \longrightarrow H_2O_2 + O_2 \qquad (8)$$

With this background, the present sonochemical results are more readily discussed.

Acrylamide.—Figure 1 shows the results obtained for hydrogen peroxide production by ultrasound in water containing acrylamide, which is known to be an efficient scavenger of H and OH radicals. The yield decreases monotonically with increasing concentration of acrylamide, both in oxygen-saturated and in argon-saturated solution. This is as expected, since the scavenging reaction 4 removes OH radicals which would otherwise produce H_2O_2 by reaction 3. A similar result has been re-

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(15) J. Frenkel, *Acta Physicochim. U.R.S.S.*, **12**, 317 (1940).

(16) N. Miller, *Trans. Faraday Soc.*, **46**, 546 (1950).

(17) W. H. Rodebush and M. H. Wahl, *J. Chem. Phys.*, **1**, 696 (1933).

(18) O. Oldenberg, *ibid.*, **3**, 266 (1935).

(19) M. E. Fitzgerald, V. Griffing and J. Sullivan, *ibid.*, **25**, 926 (1956).

(20) M. Haissinsky and A. Mangeot, *Nuovo cimento*, **4**, 1086 (1956).

(21) E. Collinson, F. S. Dainton and G. S. McNaughton, *Trans. Faraday Soc.*, **53**, 357 (1957).

(22) E. J. Hart, THIS JOURNAL, **73**, 68 (1951); *J. Phys. Chem.*, **56**, 594 (1952).

(23) P. Alexander and M. Fox, *Nature*, **170**, 1022 (1952).

(24) G. M. Eisenberg, *Ind. Eng. Chem., Anal. Ed.*, **15**, 327 (1943); A. Weissler, *ibid.*, **17**, 695 (1945).

ported in the analogous experiment with α-particles.[25]

It is evident from the two curves that, at any concentration of scavenger, more H_2O_2 is produced in oxygen-saturated than in argon-saturated solution. Qualitatively, this supports Yeager's recent finding[26] with isotopic oxygen that in oxygenated solutions only $^2/_3$ of the total sonochemical yield of peroxide is derived from OH radicals from the water; the remaining $^1/_3$ comes from the oxygen gas, by reactions 7 and 8 or the equivalent. But the fact that water saturated with helium gives only about 10% as much peroxide as with oxygen shows that, quantitatively, other factors must be involved (solubility, ionization potential, etc., of the gas).

In the argon curve, the yield decreases linearly with the log of scavenger concentration, as predicted by a simple kinetic treatment of the competition for OH radicals between scavenger and peroxide formation. The oxygen curve is clearly different; its shape fits in a general way the prediction of the radical diffusion theory,[27-29] which modifies the straightforward kinetic approach by considering also the concurrent outward diffusion (while the reactions are taking place) of the free radicals from the "hot spots" in which they are formed.

It is interesting to compare Fig. 1 with the results obtained by Collinson and co-workers[21] in air-free acrylamide solutions irradiated with X-rays. The X-ray results are in sharp contrast: the H_2O_2 yield increases rapidly with acrylamide concentration up to a maximum value (four times greater than in distilled water) at about 0.01 *M*, then falls back sharply again out to the highest concentration used, 0.5 *M*. The interpretation given is that at low concentrations the acrylamide reacts with "free" H and OH radicals which would otherwise destroy hydrogen peroxide by reactions 5 and 6, while at concentrations above 0.01 *M* it reacts also with the OH precursors of "molecular" H_2O_2 and thereby reduces the yield of reaction 3. Here then is a notable difference between the chemical effects of ultrasound and those of X-rays.

At acrylamide concentrations of 1 *M* or greater, the experimental manipulations are difficult because of the very high viscosity of the solution, due to the radical-initiated polymerization. Also, a carbylamine odor was noted after exposure to ultrasonic waves, indicating that acrylamide itself may be the source of other free radicals which undergo additional reactions.

Formic Acid.—Another set of experiments on the sonochemical production of H_2O_2, using formic acid as the scavenger in place of the acrylamide, gave the results shown in Fig. 2. The long plateau of the oxygen (upper) curve illustrates again the difference between ultrasonics chemistry and X-ray chemistry: it contrasts with a 30% increase in H_2O_2 yield found by Hart[30] over the range 10^{-4} to 1 *M* in a similar experiment with Co^{60} γ-rays and also with a 70% increase in yield observed in 10^{-3} *M* formic acid, as compared to distilled water, found for 110 kv. X-rays in an earlier study.[31] According to Hart's mechanism, these increases are due in part to suppression of back-reactions (5) and (6) by removal of radicals, and in part to the circumstance that OH radicals even if scavenged by formic acid will in the presence of oxygen eventually give H_2O_2 as a product, by the reaction

$$OH + H + HCOOH + O_2 \longrightarrow H_2O_2 + H_2O + CO_2 \quad (9)$$

But in the sonochemical reaction, no such increase is found.

The ensuing precipitous drop in Fig. 2, beginning at 0.1 mole fraction of formic acid, seems ascribable to factors which would reduce the primary production of OH radicals such as the dilu-

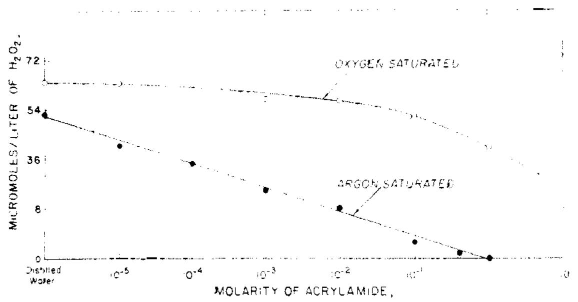

Fig. 1.—Dependence of H_2O_2 yield on acrylamide concentration.

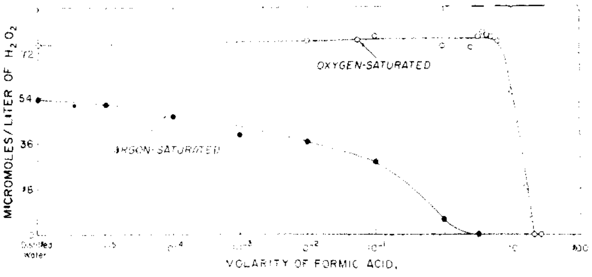

Fig. 2.—Dependence of H_2O_2 yield on formic acid concentration.

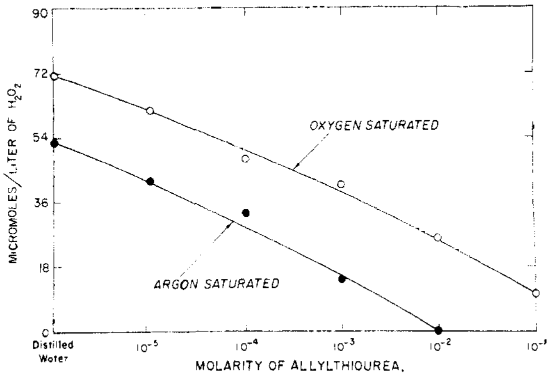

Fig. 3.—Dependence of H_2O_2 yield on allylthiourea concentration.

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(25) M. Cottin and M. Lefort, *J. chim. phys.*, **52**, 545 (1955).

(26) M. Del Duca, E. Yeager, M. O. Davies and F. Hovorka, *J. Acous. Soc. Am.*, **30**, 301 (1958).

(27) H. A. Schwarz, THIS JOURNAL, **77**, 4960 (1955).

(28) A. K. Ganguly and J. L. Magee, *J. Chem. Phys.*, **25**, 129 (1956).

(29) L. Monchick, J. L. Magee and A. H. Samuel, *ibid.*, **26**, 935 (1957).

(30) E. J. Hart, *Radiation Research*, **1**, 53 (1954).

(31) H. Fricke, E. J. Hart and H. P. Smith, *J. Chem. Phys.*, **6**, 229 (1938).

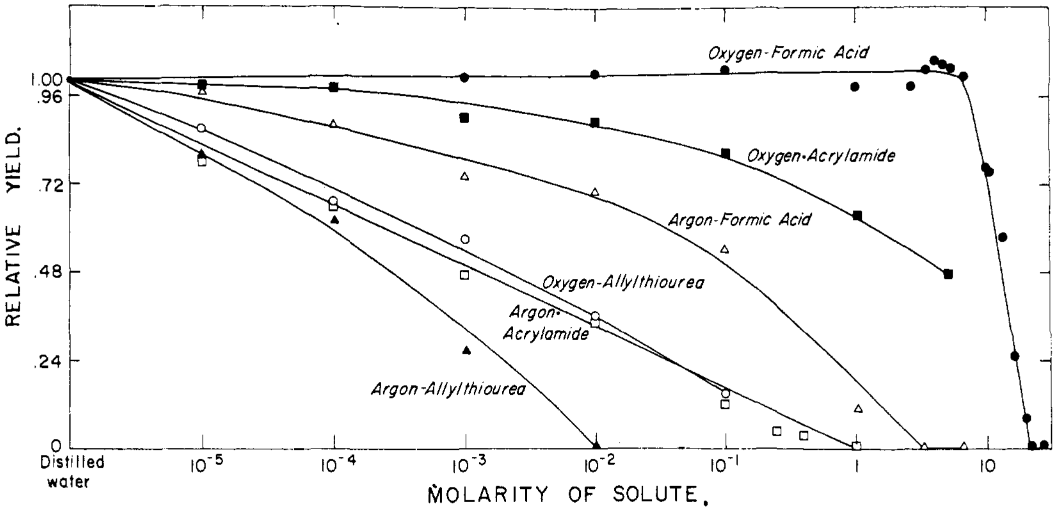

Fig. 4.—Relative yield of H_2O_2, as a function of radical-scavenger concentration.

tion of H_2O by HCOOH molecules in the cavitation bubble and perhaps also a decrease in the effectiveness of electric discharge during cavitation because of the lower dielectric constant of HCOOH–H_2O vapor mixtures in the bubble.

Turning now to the argon-saturated formic acid solutions, we find again an indication of dissimilarity between sonochemistry and radiation chemistry. The lower curve in Fig. 2 is approximately of the form predicted by the radical-diffusion theory. It is very different, however, from the experimental results for H_2O_2 yield in the 35 Mev. helium ion irradiation of acetic acid solutions,[32] either helium-saturated or degassed, in which an increase of nearly 50% in yield was found when the acetic acid concentration was increased from 0.06 to 1 *M*. This contrasts with a decrease of about 40% for the sonochemical effect in formic acid, as is evident from the curve.

If the data of Fig. 2 are replotted on ordinary rectangular (instead of semi-logarithmic) coördinates, the difference between the oxygen and argon curves is emphasized and the oxygen curve has a symmetrical shape.

Alkylthiourea.—It has been reported that allylthiourea is an efficient scavenger of HO_2 but not of OH radicals.[23] Inasmuch as HO_2 is believed to participate in one of the major routes for the radiochemical synthesis of hydrogen peroxide in oxygenated water[33]

$$H + O_2 \longrightarrow HO_2 \qquad (7)$$

$$HO_2 + HO_2 \longrightarrow H_2O_2 + O_2 \qquad (8)$$

parallel experiments were next undertaken in oxygen-saturated and in argon-saturated solutions of allylthiourea, in order to study the role of HO_2 in the sonochemical production of hydrogen peroxide.

The results, in Fig. 3, are surprising in that the rate of decrease of yield with allylthiourea concentration is just as great in argon solution as in oxygen solution. Inasmuch as the occurrence of reactions 7 and 8 or the equivalent in sonochemistry has been demonstrated in a paper[26] published after completion of the present work, it seems likely that allylthiourea is not a specific scavenger for HO_2 under these conditions. On the other hand, it was found that H_2O_2 itself is destroyed slowly by allylthiourea, especially at higher concentrations. No destruction of H_2O_2 by 1 *M* acrylamide, and only a negligible amount by 10 *M* formic acid, was observable at 40°.

A mercaptan odor was observed in the argon runs, but a carbylamine odor developed in the oxygen runs.

General Remarks.—With scavengers absent, the H_2O_2 yield is about 20% lower in argon-saturated than in oxygen-saturated water. This contrasts with one recent report[12] in which a 50% greater yield was found in argon solution, but does agree with two other findings.[2,20]

A comparison of the various radical scavengers, with respect to scavenging efficiency, may be seen in Fig. 4, which shows relative yield of peroxide (observed yield divided by yield at zero concentration of scavenger) as a function of scavenger concentration. One feature of the curves is that the percentage efficiency of any scavenger is less in oxygen than in argon solution. In this connection, if the observed yield of H_2O_2 in oxygenated solutions represents the sum of two separate though interrelated processes (the combination of hydroxyl radicals in pairs, and the combination of H with O_2 followed by disproportionation of the HO_2 radicals), a scavenger may affect one of these more than the other.

Notable also in Fig. 4 is that formic acid is the least efficient of the three scavengers, even though it is the most volatile. This result is unexpected, because the major sonochemical reactions are ordinarily believed to occur in the vapor phase inside the cavitation bubble. However, other recent results[26] suggest that the secondary reactions responsible for the sonochemical formation of hydrogen peroxide take place at least partly in the liquid phase.

The experiments described above constitute evidence that OH radical is an intermediate in

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(32) W. M. Garrison, W. Bennett, S. Cole, H. R. Haymond and B. M. Weeks, This Journal, **77**, 2720 (1955). This was chosen for comparison as an example of heavy-particle effects, even though the conditions are only partly comparable.

(33) C. J. Hochanadel, *J. Phys. Chem.*, **56**, 587 (1952).

the sonochemical production of hydrogen peroxide. It appears that there are differences between peroxide formation due to ionizing radiation and that due to ultrasonic cavitation, but further work is required to clarify the differences.

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BETHESDA 14, MARYLAND

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF WASHINGTON]

The Isomerization of Vibrationally Excited Cyclopropane-d_2 Produced from Methylene plus Ethylene-d_2[1]

BY B. S. RABINOVITCH, E. TSCHUIKOW-ROUX AND E. W. SCHLAG

RECEIVED SEPTEMBER 3, 1958

Vibrationally excited cyclopropane-d_2 molecules have been produced at 25° by addition of methylene radicals, arising from photolysis of ketene at 3600 and 3100 Å., to *trans*-ethylene-d_2. The addition is stereospecifically *cis*. The geometric and structural isomerization of the hot cyclopropane molecules has been studied at pressure up to 36 atm. Comparison of these results with thermal studies, and between themselves, provides support for similarity of activation steps for the two isomerization processes.

trans-Cyclopropane-d_2 has been observed to isomerize thermally to *cis*-cyclopropane-d_2 as well as to propylene.[2] The former reaction has been shown to occur as a unimolecular process while the latter is known to be such.[3] The mechanisms of the geometric *cis-trans* isomerization and structural isomerization to propylene may involve either of the two molecular reaction coordinates suggested originally by Chambers and Kistiakowsky[3a]; namely a C–C extension, or an approach of a hydrogen on one carbon atom to an adjacent carbon.[4] Whatever mechanism may apply, the results of Rabinovitch, Schlag and Wiberg suggest that the activated complexes for both geometric and structural isomerization are similar, particularly energy-wise. The present study was undertaken to test this point in another way, by measuring the relative rates of the two isomerization processes at a range of energies appreciably different (higher) from those accessible in the thermal study.

Kistiakowsky and Sauer[5] pointed out that vibrationally excited cyclopropane is formed on addition of methylene to ethylene. Frey[6a] reported the isolation of cyclopropane and propylene as principal products of the photolysis of ketene–ethylene mixtures, and Frey and Kistiakowsky[6b] presented quantitative studies of the variation of product proportions with total pressure. In the present work, by use of *trans*-ethylene-d_2 the stereochemistry of the addition process has been determined and the rate of geometric *cis–trans* isomerization of the vibrationally excited cyclopropane-d_2 has been measured and compared with that of the concomitant structural isomerization to propylene.

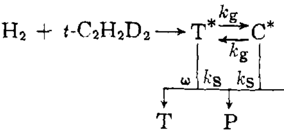
Experimental

trans-Ethylene-d_2 was of 99.3% isotopic purity with 0.7% ethylene-d_1. Ketene was purified by repeated bulb-to-bulb distillation. Mass spectrometric analysis showed the ketene to be essentially pure with negligible amounts of the dimer.

Photolysis of ketene–ethylene-d_2 mixtures was carried out in sealed reactors at 25°. A General Electric AH-6 high pressure mercury arc lamp served as the light source. The bands at 3100 and 3600 Å. were employed. A Corning glass filter No. 5330 was employed to isolate the 3600 Å. region and a solution filter, made by dissolving $NiSO_4 \cdot 6H_2O$ and $CoSO_4 \cdot 7H_2O$ in water,[7] was used at 3100 Å. The solution was circulated through a Corex D glass envelope in front of the lamp. The reactor was of Corex glass as well for the study at 3100 Å., while Pyrex vessels were employed at 3600 Å. A range of pressures of 0.14 to 36.6 atm. was covered. In each case the ratio of ketene/ethylene-d_2 was close to 1/7. The amount of ketene varied from 2–20 cc. per run, while the ketene decomposition varied from 1–20% in most cases, and up to 40% in a few cases. Some polymerization was observed which, however, only became appreciable for the runs at the highest pressures which necessitated the longest exposure times (up to 35 min.). At the end of each run the excess ethylene-d_2 was pumped off at −160°. The remaining gases were then distilled through a column of brick-dust covered with a saturated solution of $AgNO_3$ in ethylene glycol and Kel-F alkane oil. This effectively removed the remaining ketene. The cyclopropane–propylene mixture was analyzed and separated by gas chromatography, and the cyclopropane was analyzed for the percent *cis* and *trans*-cyclopropane-d_2 on a Beckman IR-2 spectrophotometer by methods used previously.[2]

Results and Discussion

Relevant processes are represented by the scheme where T, C and P refer to *trans*-cyclopropane-d$_2$, *cis*-cyclopropane-d_2 and propylene, respectively.



Here k_g and k_s refer to the observed rate constants and the above scheme carries no further implication

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[1] This research was supported by the National Science Foundation. Abstracted from the M.S. Thesis of E. Tschuikow-Roux, University of Washington, Feb., 1958.

[2] Rabinovitch, Schlag and Wiberg, *J. Chem. Phys.*, **28**, 504 (1958).

[3] (a) T. S. Chambers and G. B. Kistiakowsky, THIS JOURNAL, **56**, 399 (1934); (b) H. O. Pritchard, R. G. Sowden and A. F. Trotman-Dickenson, *Proc. Roy. Soc.* (*London*), **A217**, 563 (1953); (c) N. B. Slater, *ibid.*, **A218**, 224 (1953).

[4] These are extremes, and an intermediate type of coördinate could also be considered. See also F. T. Smith, *J. Chem. Phys.*, **29**, 235 (1958).

[5] G. B. Kistiakowsky and K. Sauer, THIS JOURNAL, **78**, 5699 (1956).

[6] (a) H. M. Frey, *ibid.*, **79**, 1259 (1957); (b) H. M. Frey and G. B. Kistiakowsky, *ibid.*, **79**, 6373 (1957).

[7] W. A. Noyes and P. A. Leighton, "Photochemistry of Gases," Reinhold Publ. Corp., New York, N. Y., 1941, p. 69; E. J. Bowen, *J. Chem. Soc.*, 76 (1935).