the homologous series of straight-chain amine hydrochlorides, as determined by conductivity measurements by Ralston and Hoerr,[11] are plotted in Figure 4, and a straight-line relationship, in accordance with eq 8, was obtained

$$\log \mathrm{cmc} = 1.252 - 0.265n \qquad (9)$$

If the values obtained for the cmc of dodecylamine hydrochloride from Figure 3 are introduced in eq 9, the values of n calculated for the paraffinic gases result: ethane, $n = 12.35$; propane, $n = 12.80$. *I.e.*, this is 0.35 unit of $-CH_2-$ for ethane and 0.80 for propane, in close agreement with the values calculated previously from surface tension considerations.

Acknowledgment. This work is part of I. J. Lin's D. Sc. (Tech) Thesis to the Technion, Israel Institute of Technology, Haifa.

The Reactions of Acetone and Hydrogen Peroxide. I. The Primary Adduct[1]

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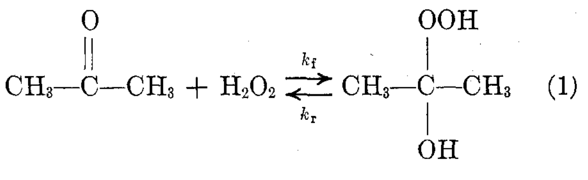
The reaction between acetone and hydrogen peroxide leads to 2-hydroxy-2-hydroperoxypropane as a first product. The equilibrium constant of formation of this compound was found to be $K = 0.086\ M^{-1}$ at 25°. Thermodynamic parameters of the reaction are $\Delta H = -7.0$ kcal mol^{-1} and $\Delta S = -28$ cal mol^{-1} deg^{-1}. The kinetics of formation and dissociation of 2-hydroxy-2-hydroperoxypropane were studied by both uv spectroscopy and nmr line-broadening techniques. The reaction exhibits general acid and base catalysis. Values of the Brønsted parameters α and β were obtained. The variation of the base-catalyzed rate constants k_{OH} with temperature were studied by the nmr line-broadening technique. Values of activation enthalpy (1.7 kcal mol^{-1}) and entropy of activation (-18 cal mol^{-1} deg^{-1}) were obtained for the forward reaction; corresponding values for the reverse reaction were found to be 8.7 kcal mol^{-1} and $+10$ cal mol^{-1} deg^{-1}.

Introduction

The reaction between acetone and hydrogen peroxide in aqueous solution was studied by several investigators and different products were isolated and identified.[2] However, the product that results from the addition of 1 mol of hydrogen peroxide to acetone, that is 2-hydroxy-2-hydroperoxypropane (compound I), was not detected until recently.[1,3] This compound has, however, been isolated from the photosensitized oxidation of isopropyl alcohol.[4]



$$CH_3-\overset{\overset{\displaystyle O}{\|}}{C}-CH_3 + H_2O_2 \underset{k_r}{\overset{k_f}{\rightleftarrows}} CH_3-\overset{\overset{\displaystyle OOH}{|}}{\underset{\underset{\displaystyle OH}{|}}{C}}-CH_3 \qquad (1)$$

I

We have found considerable evidence for the existence of this compound in solutions of acetone and hydrogen peroxide. Studies of the thermodynamics and kinetics of its formation determine the experimental conditions under which detection and isolation of this compound may be possible. The quantitative solution data are presented in this article.

Experimental Section

Materials. Reagent grade acetone was used without further purification. Hydrogen peroxide [50% (w/w) and 90% (w/w) donated by the FMC Corp. and 30% (w/w) from Allied Chemical] was used in making peroxide solutions. Reagent grade inorganic salts were used as obtained. Organic acids and their salts were either distilled or recrystallized before use.

Analytical. The total peroxide was determined. A known volume of dilute sample was added to 10 ml of water, 1 ml of sulfuric acid (1/1), and 2 g of KI. In the analysis of acetone–hydrogen peroxide mixtures, acetic acid was used instead of water. Ammonium molybdate was added as a catalyst. The solution was allowed to

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(1) Abstracted from part of the Ph.D. Thesis of M. C. V. Sauer at Brown University, June 1970.

(2) A. Rieche, *Angew. Chem., Int. Ed. Engl.*, **70**, 251 (1958); (b) N. A. Milas and A. Golubovic, *J. Amer. Chem. Soc.*, **81**, 6461 (1959).

(3) J. Hine and R. W. Redding, *J. Org. Chem.*, **35**, 2769 (1970).

(4) G. O. Schenk and H. D. Becker, *Angew. Chem., Int. Ed. Engl.*, **70**, 504 (1958).

stand for a few minutes and then the resultant iodine was titrated with standard sodium thiosulfate. The concentration of hydrogen peroxide in the mixtures with acetone was also checked using the same method. No appreciable difference in concentration was found between the value obtained from the titration and the value calculated from dilution with a known volume of acetone.

Equipment. A Varian A-60A nmr spectrometer was used. The temperature of the probe was set using the variable-temperature accessory attached to the spectrometer and was checked using the calibration determined from the separation of the two resonances of methanol.[5]

A Cary 14 recording spectrometer with chart speeds up to 8 in. min^{-1} was used for kinetic determinations. Measurements of pH were made with a Leeds and Northrup pH meter using glass electrodes standardized with commercial buffers. The pH values were corrected for effect of the H_2O_2 on the glass electrode readings.[6]

Equilibrium Constants by Nmr. All of the mixtures were prepared in a test tube and then a small volume was transferred to an nmr tube. This two-stage procedure was found to be optimum for complete mixing of the reactants. The samples were thermostated before the spectra were recorded.

Kinetic Measurements. In the uv spectroscopy runs, the rate was followed by measuring the decrease in carbonyl absorption at 275 nm. The reactions were initiated by the addition with a syringe of 1 ml of the thermostated acetone solution to 2 ml of the hydrogen peroxide solution previously placed in a cell and equilibrated at fixed temperature in the cell compartment of the spectrometer. A minimum of 4 sec was required before absorbance recordings could be obtained with this technique. The effect of hydrogen peroxide concentration on the glass electrode pH readings was very small in the range of concentrations of the uv kinetic runs,[6] so no corrections were applied unless noted otherwise. The ionic strength was maintained at 1 M by addition of KCl. The concentration of the acidic component of each buffer was calculated from the relationships

$$\frac{K_a}{[\mathrm{H}^+]} = \frac{[\mathrm{B}]}{[\mathrm{AH}]}$$

and

$$[\mathrm{B}] + [\mathrm{AH}] = C_0$$

so

$$[\mathrm{AH}] = \frac{C_0[\mathrm{H}^+]}{K_a + [\mathrm{H}^+]}$$

where C_0 is the buffer concentration, AH is the free buffer acid, B is the conjugate base of the buffer, K_a is the ionization constant of the buffer acid, and brackets are employed to denote concentration.

Nmr Line-broadening. The nmr lines were recorded on slow passage, and the width was measured from the recording. The effective T_2 obtained was then used to correct the measured line width of the samples with appreciable chemical exchange. The difference was attributed to exchange broadening. Before and after every measurement, a sample at the same concentration but on conditions of negligible chemical exchange (that is, lower pH) was recorded and the line width measured.

Results

Thermodynamics. The proton magentic resonance (nmr) spectra of aqueous mixtures of acetone and hydrogen peroxide were studied in the ranges of acetone concentration from 3.8 to 10 M and hydrogen peroxide concentration from 5 to 13 M. From the proton nmr spectra of aqueous acetone the chemical shifts of the methyl resonance of acetone and the proton resonance of water were found to be δ 2.23 and 5.48 with respect to the internal reference tetramethylsilane. The chemical shifts vary slightly with the acetone concentration.

The nmr spectrum of a freshly prepared mixture of acetone and hydrogen peroxide consists of two low-field signals at δ 2.23 and 1.43 and a very broad high-field signal at about δ 5. The high-field resonance corresponds to the protons of H_2O, H_2O_2, and –OH and –OOH groups exchanging very rapidly to produce a single resonance line which has a position established by the natures and relative concentrations of the involved species. The δ 1.43 resonance was assigned to the methyl protons of the addition product; this assignment is consistent with the line positions for known acetal-like species.[1,3]

In order to confirm the assumed stoichiometry the equilibrium position of the reaction was studied at several reactant ratios. Concentrations of acetone and 2-hydroxy-2-hydroperoxypropane (adduct) at equilibrium were found by integrating both resonances and are given by the following equations

$$[\text{acetone}]_e = \frac{I_{\mathrm{Ac}}}{I_{\mathrm{Ac}} + I_{\mathrm{AP}}}[\text{acetone}]_0$$

$$[\text{adduct}]_e = \frac{I_{\mathrm{AP}}}{I_{\mathrm{Ac}} + I_{\mathrm{AP}}}[\text{acetone}]_0$$

where I_{Ac} and I_{AP} are the integrated areas representing acetone and adduct and the subscripts 0 and e represent initial state and equilibrium state, respectively. The hydrogen peroxide concentration at equilibrium was found by the mass relation

$$[\mathrm{H_2O_2}]_e = [\mathrm{H_2O_2}]_0 - [\text{adduct}]_e$$

The equilibrium constants were found using the relation

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(5) "Varian A-60A NMR Spectrometer System Manual," pp 4–12.

(6) J. R. Kolczinski, E. M. Roth, and E. S. Shanley, *J. Amer. Chem. Soc.*, **79**, 531 (1957).

$$K = \frac{[\text{adduct}]_e}{[\text{acetone}]_e[H_2O_2]_e}$$

Each value of K reported in Table I is an average of at least four determinations. The thermodynamic parameters at 25° of the reaction are ΔG = 1.47 kcal mol^{-1}, ΔH = −7.0 kcal mol^{-1}, ΔS = −28 cal mol^{-1} deg^{-1}, and $T\Delta S$ = −8.5 kcal mol^{-1}.

Table I: Equilibrium Constants for the Primary Addition Reaction of Acetone and Hydrogen Peroxide at Different Temperatures

Temp, °C	K, M^{-1}
0.0 ± 0.5	0.23 ± 0.02
6.0	0.19 ± 0.02
12.0	0.14 ± 0.02
22.0	0.093 ± 0.02
27.0	0.078 ± 0.02
32.0	0.064 ± 0.03
42.0	0.042 ± 0.03

Kinetics by Uv Spectroscopy. The kinetics of reaction 1 were studied spectrophotometrically by following the decrease in carbonyl absorption at 275 nm in a range of acetone concentration from 0.09 to 0.13 M and hydrogen peroxide concentration from 0.31 to 0.62 M. Although the equilibrium constant of the reaction is small, it was found that by using an excess of hydrogen peroxide, the change in the absorbance was significant and the reaction proceeds at a measurable rate.

It was expected that the rate law would, at least insofar as the reactants were concerned, reflect the stoichiometry

$$\frac{-d[\text{acetone}]}{dt} = k_f[\text{acetone}][H_2O_2] - k_r[\text{adduct}]$$

When hydrogen peroxide is in considerable excess, the rate should follow pseudo-first-order kinetics. Using a to represent acetone absorption and the a_0, a_t, and a_e to denote initial absorption, absorption at time t, and absorption at equilibrium, respectively, the data can be treated by the equation[7]

$$-\log\left(\frac{a_t - a_e}{a_0 - a_e}\right) = k_{\text{obsd}}t$$

If k_f and k_r represent the forward and reverse rate constants, we know that

$$2.303k_{\text{obsd}} = k_f[H_2O_2] + k_r$$

Using the principle of microscopic reversibility

$$K = \frac{k_f}{k_r}$$

then

$$k_r = \frac{2.303k_{\text{obsd}}}{K[H_2O_2] + 1}$$

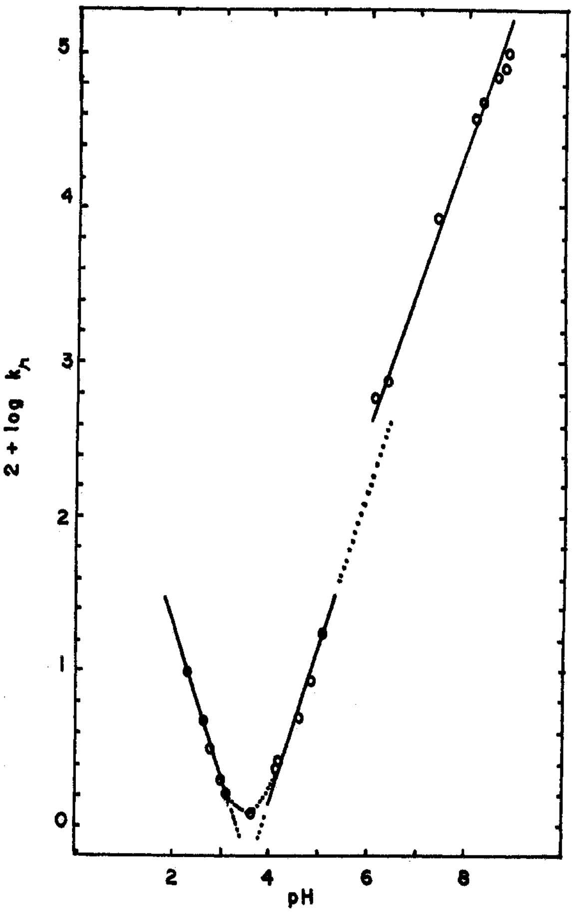

Figure 1. The dependence of rate of dissociation of 2-hydroxy-2-hydroperoxypropane on pH at 25°: pH 2–5, uv spectroscopy, [acetone] = 0.09–0.13 M, [H_2O_2] = 0.31–0.62 M; pH 6–9, nmr line-broadening technique, [acetone] = 0.62–1.42 M, [H_2O_2] = 8–20 M.

Values of K obtained by nmr were used in calculation of k_r and the k_f.

In the absence of any undissociated acid or base, the rate constant in either direction can be expressed as a sum of terms

$$k = k_0 + k_H[H^+] + k_{OH}[OH^-]$$

The pH dependence of the observed rate of adduct dissociation in the absence of general acids and bases is shown in Figure 1. At low pH, the appropriate expression is

$$\log k = \log k_H - \text{pH}$$

and a plot of log k *vs.* pH is a straight line with slope −1. From this line a value of k_H can be calculated. In the same way, the expression for basic solutions is

$$\log k = \log k_{OH} + \log [OH^-]$$

and a value of k_{OH} can now be calculated from the right-hand line of the plot.

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[7] A. A. Frost and R. G. Pearson, "Kinetics and Mechanism," 2nd ed, Wiley, New York, N. Y. 1965, p 218.

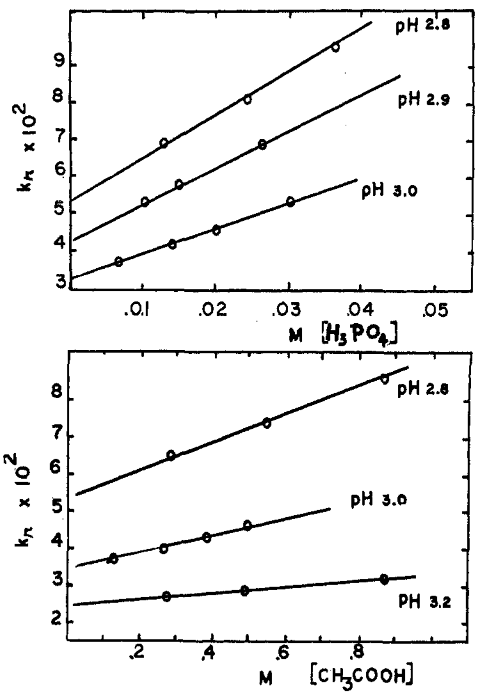

Figure 2. Dependence of rate of dissociation on concentration of buffer acid at 25°.

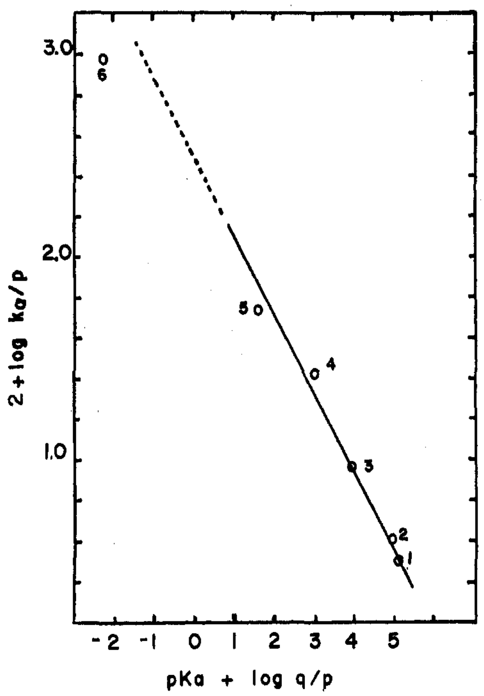

Figure 3. Brønsted plot for acid catalysis of dissociation at 25°. Buffer acids are designated: 1, propionic acid; 2, acetic acid; 3, formic acid; 4, chloroacetic acid; 5, phosphoric acid; and 6, hydronium ion.

These data give second-order rate constants (based on the hydrogen and hydroxide ion concentrations of the figure) of $k_{\mathrm{H,r}} = 33.8\ M^{-1}\ \mathrm{sec}^{-1}$ and $k_{\mathrm{OH,r}} = 1.88 \times 10^8\ M^{-1}\ \mathrm{sec}^{-1}$ for the dissociation of 2-hydroxy-2-hydroperoxypropane and third-order rate constants of $k_{\mathrm{H,f}} = 2.9\ M^{-2}\ \mathrm{sec}^{-1}$ and $k_{\mathrm{OH,f}} = 1.6 \times 10^7\ M^{-2}\ \mathrm{sec}^{-1}$ for the formation of the adduct.

The difference between the observed rate and that calculated for the sum of the acid- and base-catalyzed reactions at the pH rate minimum indicates that there is a water-catalyzed path for this reaction with a second-order rate constant $k_{\mathrm{H_2O,r}} = 3 \times 10^{-5}\ M^{-1}\ \mathrm{sec}^{-1}$ for adduct dissociation.

The general acid–base catalysis was studied with five different acids and their conjugate bases at increasing buffer concentrations and several buffer ratios. The rate data can be treated using the equation

$$k = k_0 + k_{\mathrm{H}}[\mathrm{H}^+] + k_{\mathrm{OH}}[\mathrm{OH}^-] + k_{\mathrm{a}}[\mathrm{AH}] + k_{\mathrm{b}}[\mathrm{B}]$$

At a given pH

$$\frac{[\mathrm{AH}]}{[\mathrm{B}]} = \frac{[\mathrm{H}^+]}{\mathrm{K_a}} = \theta$$

is a constant; then

$$[\mathrm{B}] = \frac{[\mathrm{AH}]}{\theta}$$

and the rate constant expression becomes

$$k = k_0 + k_{\mathrm{H}}[\mathrm{H}^+] + k_{\mathrm{OH}}[\mathrm{OH}^-] + (k_{\mathrm{a}} + k_{\mathrm{b}}/\theta)[\mathrm{AH}]$$

A plot of k against [AH] at a given pH should be a straight line with slope $k_{\mathrm{a}} + k_{\mathrm{b}}/\theta$. It is clear that at several ratios [AH]/[B], in buffers at different pH, we should have different slopes when k is plotted against free acid concentration.

Figure 2 shows a plot of k_{r} against conjugate acid concentration for phosphoric acid buffers and acetic acid buffers. In Table II are shown the catalytic constants $k_{\mathrm{a,r}}$, and $k_{\mathrm{b,r}}$ for the reverse reaction and $k_{\mathrm{a,f}}$ and $k_{\mathrm{b,f}}$ for the forward reaction. The rate constants for the general acid and base catalysis followed the Brønsted law as can be seen in Figures 3 and 4. The parameters α and β were obtained from the figures and they are $\alpha = 0.43$ and $\beta = 0.50$ for the reverse reaction and $\alpha = 0.53$ and $\beta = 0.55$ for the forward reaction.

Line-Broadening Kinetics. It was observed that, due to the magnitude of the base catalysis, a study of the kinetics of the addition reaction by the nmr line-broadening technique would be possible at pH values higher than 6 and in concentrated solutions of hydrogen peroxide. The chemical exchange was studied in a range of acetone concentration from 0.62 to 1.42 M and hydrogen peroxide concentration from 8 to 20 M. Figure 5 shows the broadening of the methyl proton resonances for acetone and for the addition product as the pH is increased. The half-widths of the lines and the theory developed by Gutowsky, McCall, and Schlichter[8] were used to evaluate the exchange rates.

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(8) J. A. Pople, W. G. Schneider, and J. H. Bernstein, "High-Resolution Nuclear Magnetic Resonance," McGraw-Hill, New York, N. Y., 1959, Chapter 10.

Table II: Catalytic Rate Constants for Dissociation and Formation of Adduct with General Acids and Their Conjugate Bases at 25° and $\mu = 1$

Acid	$k_{a,r}$, M^{-1} sec^{-1}	$k_{b,r}$, M^{-1} sec^{-1}	$k_{a,f}$, M^{-2} sec^{-1}	$k_{b,f}$, M^{-2} sec^{-1}
H_3O^+	33.8	(1.5×10^{-5})[a]	2.90	(1.3×10^{-6})[b]
H_3PO_4	1.63	2.7×10^{-2}	0.14	2.3×10^{-3}
$ClCH_2COOH$	0.27	5.7×10^{-2}	2.3×10^{-2}	4.9×10^{-3}
HCOOH	9.4×10^{-2}	0.13	8×10^{-3}	1.1×10^{-2}
CH_3COOH	4.3×10^{-2}	0.50	4×10^{-3}	4.3×10^{-2}
CH_3CH_2COOH	3.3×10^{-2}	0.58	3×10^{-3}	4.9×10^{-2}
H_2O	(1.5×10^{-5})[a]	1.88×10^{8}	$(1.3 \times 10^{6-})$[b]	1.08×10^{7}

[a] Assignment is presently ambiguous since H_2O can act as an acid, as a base, or as both. [b] Also an ambiguous assignment.

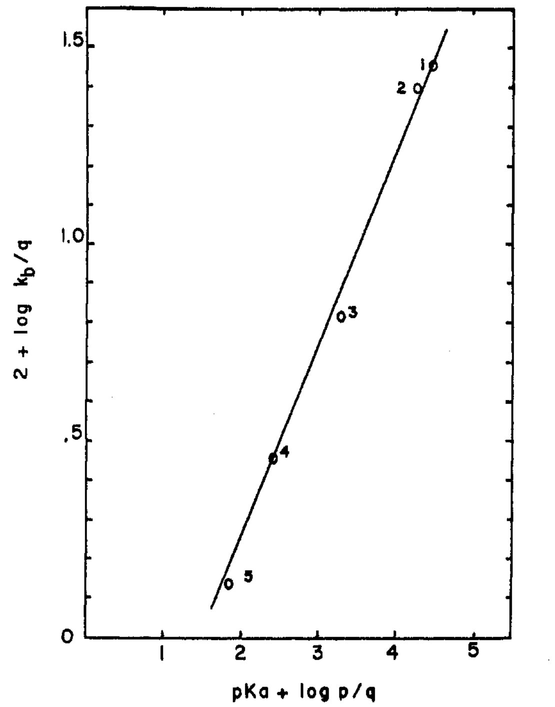

Figure 4. Brønsted plot for base catalysis of dissociation at 25°. Numbers designate conjugate bases of acids listed in Figure 3.

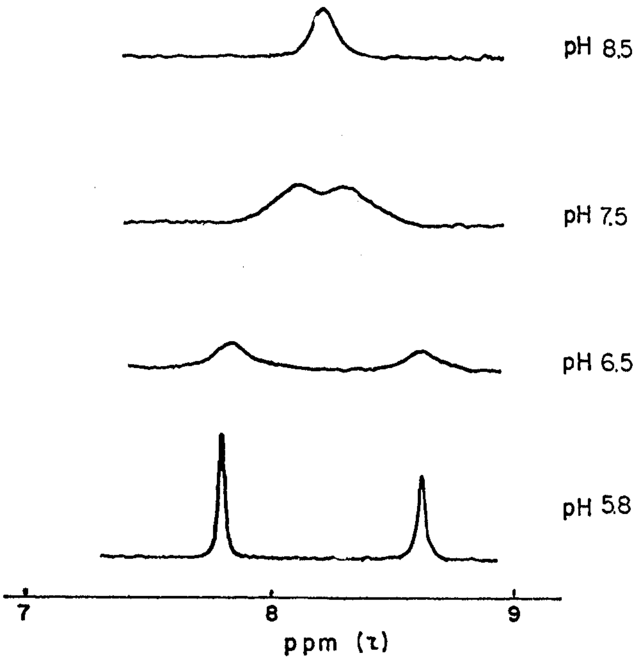

Figure 5. Effect of pH on nmr line width of proton resonances for acetone and 3-hydroxy-2-hydroperoxypropane; sweep time 250 Hz, sweep width 500 Hz, and probe temperature −40°.

When the spectrum consists of two isolated lines of acetone and adduct ("slow exchange"), it can be shown[8] that the individual line widths $\Delta\nu$ (full line width at half-height) are related to the rate constants by the equations

$$\tau_{Ac} = 1/\pi(\Delta\nu'_{Ac} - \Delta\nu_{Ac}) = 1/k_f[H_2O_2]$$

and

$$\tau_{AP} = 1/\pi(\Delta\nu'_{AP} - \Delta\nu_{AP}) = 1/k_r$$

where the $[H_2O_2]$, because it is present in considerable excess with respect to acetone, remains constant. In these equations, τ_{Ac} and τ_{AP} represent the mean lifetimes of the protons of acetone and 2-hydroxy-2-hydroperoxypropane, $\Delta\nu'_{Ac}$ and $\Delta\nu'_{AP}$ the line widths of the acetone and adduct resonances in the presence of exchange, and $\Delta\nu_{Ac}$ and $\Delta\nu_{AP}$ line widths of the acetone and adduct resonances in the absence of exchange.

At the point where both resonances coalesce ("intermediate exchange") calculations can be made using the equation

$$\tau = \left[\frac{1}{1 - \left(\dfrac{\Delta\nu_{Ac} - \nu_{AP}}{\nu_{Ac} - \nu_{AP}}\right)^2 2\pi^2(\nu_{Ac} - \nu_{AP})^2}\right]^{1/2}$$

along with the definition

$$\tau = \frac{\tau_{Ac}\tau_{AP}}{\tau_{Ac} + \tau_{AP}} = p_{Ac}\tau_{AP}$$

and from this we can calculate $1/\tau_{Ac}$ and $1/\tau_{AP}$.

When the rate of exchange is relatively rapid, the two lines overlap and a single resonance line is observed ("fast exchange"), centered on a weighted-mean frequency ω(mean). If we define

$$p_{Ac} = \tau_{Ac}/(\tau_{Ac} + \tau_{AP}) \text{ and } p_{AP} = \tau_{AP}/(\tau_{Ac} + \tau_{AP})$$

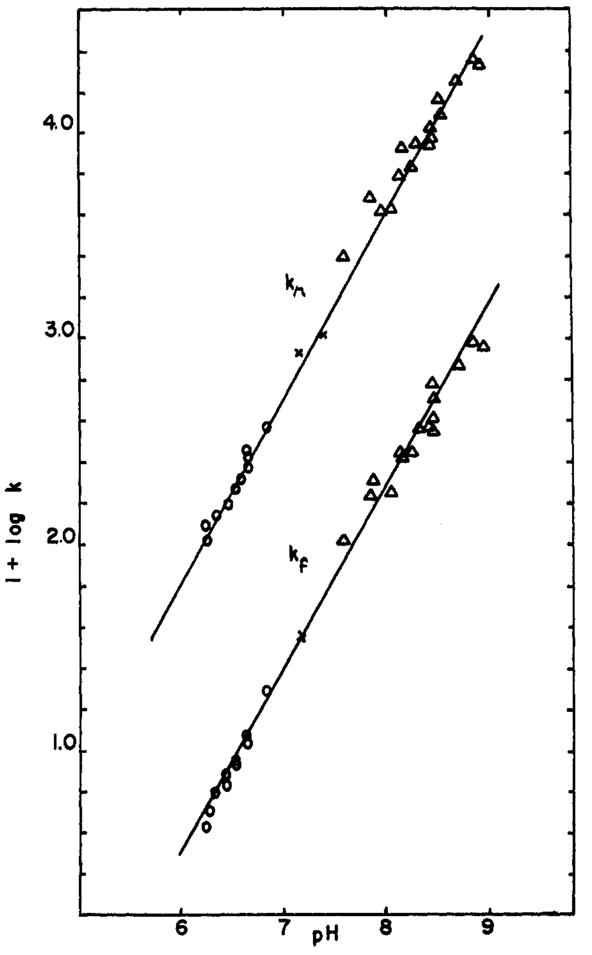

Figure 6. Rate data for dissociation (k_r) and formation (k_f) of 2-hydroxy-2-hydroperoxypropane taken by nmr line-broadening technique at 40°. Lines are drawn with a slope of 1. Circles are for slow exchange region, crosses for intermediate exchange region, and triangles are for fast exchange region.

then, $\omega(\text{mean}) = p_{Ac}\omega_{Ac} + p_{AP}\omega_{AP}$ where $\omega_{Ac}/2\pi$ and $\omega_{AP}/2\pi$ represent the Larmor frequencies of protons Ac and AP in cycles/sec. The half-width of the single line $\Delta\nu'$ now is related to the lifetimes of the protons of acetone and the adduct as follows

$$\pi\Delta\nu' = p_{Ac}\Delta\nu_{Ac} + p_{AP}\Delta\nu_{AP} + p_{Ac}{}^2p_{AP}{}^2(\omega_{Ac} - \omega_{AP})^2(\tau_{Ac} + \tau_{AP})$$

From this it can be shown that

$$\frac{1}{\tau_{Ac}} = \frac{p_{Ac}(1 - p_{Ac})^2(\nu_{Ac} - \nu_{AP})4}{\pi\Delta\nu' - \pi p_{Ac}\Delta\nu_{Ac} - \pi\Delta\nu_{AP}(1 - p_{Ac})} = k_f[H_2O_2]$$

with $1/\tau_{AP} = p_{Ac}/(1 - p_{Ac})$ and $1/\tau_{Ac} = k_r$.

The chemical exchange between acetone and adduct was studied at four different temperatures in the range of pH 6–9. Figure 6 shows the dependence of log k_f and log k_r on pH; as can be seen, the variation is represented by a straight line of slope equal to unity.

Values of $k_{OH,f} = k_f/[OH^-]$ and $k_{OH,r} = k_r/[OH^-]$ were found at each temperature, and they are listed in Table III. Relevant activation parameters are given in Table IV.

Table III: Base-Catalyzed Rate Constants of Adduct Formation and Dissociation at Four Temperatures

Temp, °C	$k_{OH,f} \times 10^{-7}$, M^{-2} sec^{-1}	$k_{OH,r} \times 10^{-8}$, M^{-1} sec^{-1}
0	0.90	0.41
12	1.11	0.86
25	1.50	1.81
40	1.61	3.62

Table IV: Activation Parameters for Base-Catayzed Reactions

	E_a, kcal mol^{-1}	$\Delta H^{\ddagger}$, kcal mol^{-1}	$\Delta S^{\ddagger}$, cal mol^{-1} deg^{-1}
Forward reaction	2.4	1.8	−18
Reverse reaction	9.2	8.6	10

Discussion

The small equilibrium constants for formation of 2-hydroxy-2-hydroperoxypropane (K = 0.23 at 0°) as compared with the equilibrium constant for formation of the analogous adduct from acetaldehyde and hydrogen peroxide (K = 48)[9] can be attributed to the additional methyl group of acetone. The electron deficiency at the carbonyl carbon is partially compensated by the electron-releasing nature of the methyl group (as compared with hydrogen). Consequently, the stability of acetone adducts with nucleophilic reagents is expected to be lower than the stability of acetaldehyde adducts. A small steric effect (methyl *vs.* hydrogen) would work in the same direction as the electronic effect.

The thermodynamic parameters for formation of this adduct are reasonable for an addition reaction similar to the hydration of a carbonyl carbon.[10] For example, formation of a single particle from two reactants would be expected to show a negative entropy, and this is observed ($\Delta S = -28$ cal mol^{-1} deg^{-1}).

The equilibrium constants for formation of the adduct describe the system quite precisely in certain ranges of concentration studied; nevertheless other equilibria must be considered. An influence of the secondary reaction

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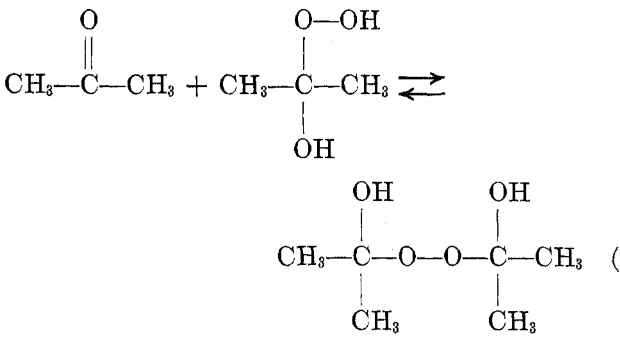
[9] P. L. Kooijman and W. L. Shijsen, *Recl. Trav. Chim. Pays-Bas*, **66**, 205 (1947).

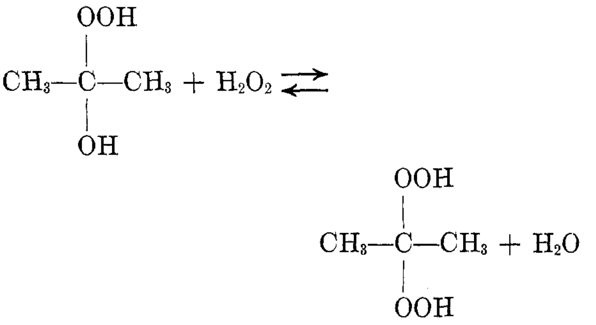
[10] R. P. Bell, *Advan. Phys. Org. Chem.*, **4**, 1 (1966).



$$CH_3-\overset{\displaystyle O}{\overset{\|}{C}}-CH_3 + CH_3-\underset{\displaystyle OH}{\overset{\displaystyle O-OH}{C}}-CH_3 \rightleftarrows CH_3-\underset{\displaystyle CH_3}{\overset{\displaystyle OH}{C}}-O-O-\underset{\displaystyle CH_3}{\overset{\displaystyle OH}{C}}-CH_3 \quad (2)$$

would be expected in solutions rich in acetone. However, there was no apparent effect of the variation in acetone concentration on the equilibrium constants in the range of concentrations studied.

At the pH (about 5) of the solutions without additives (catalysts, buffers, etc.), the formation of 2,2-bis(hydroperoxy)propane is negligible during the first hour after mixing of the reactants



$$CH_3-\underset{\displaystyle OH}{\overset{\displaystyle OOH}{C}}-CH_3 + H_2O_2 \rightleftarrows CH_3-\underset{\displaystyle OOH}{\overset{\displaystyle OOH}{C}}-CH_3 + H_2O \quad (3)$$

An independent check of the equilibrium constant (K) of the primary addition reaction between acetone and hydrogen peroxide can be obtained from the line-broadening data. Applying the principle of microscopic reversibility to the forward and reverse rate constants obtained separately under conditions of slow exchange, the equilibrium constant for the reaction can be calculated at each temperature. Further, under conditions of rapid exchange, the following equation can be applied

$$\omega_{\text{mean}} = \omega_{\text{Ac}}p_{\text{Ac}} + \omega_{\text{AP}}p_{\text{AP}}$$

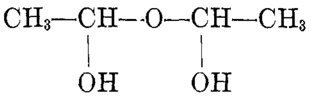
where

$$p_{\text{Ac}} = \frac{1}{1 + K[H_2O_2]}$$

and

$$p_{\text{AP}} + \frac{K[H_2O_2]}{1 + K[H_2O_2]}$$

and a new value for K can be found. Table V shows the constants obtained in each case. As can be seen, the K values found by the mean frequency equation agree with the ones previously determined, considering the much lower concentrations in acetone used in the line-broadening technique. The values k_f/k_r are in agreement with the others at temperatures equal to and above 12°. However, the value at 0° seems to be lower than the K determined by the two other techniques. Given that this number is based on only two runs under slow exchange conditions, a low K value could be explained if the reaction 2 is considered. The formation of this new compound might cause an additional broadening of the 2-hydroxy-2-hydroperoxypropane resonance, and this would be reflected in a higher k_r value. This effect is more noticeable at low temperature where the 2-hydroxy-2-hydroperoxypropane concentration is higher and the equilibrium constant for this secondary stage becomes more important as happens with all the hydroperoxide additions to carbonyl compounds. In the hydration of acetaldehyde, the adduct



$$CH_3-\underset{\displaystyle OH}{CH}-O-\underset{\displaystyle OH}{CH}-CH_3$$

was detected by nmr line-broadening at high concentrations of acetadehyde.[11] It is concluded that a study of the chemical exchange at high acetone concentrations might lead to the detection of the adduct formed from one hydrogen peroxide and two acetone molecules.

Table V: Equilibrium Constants of Adduct Formation Obtained by Different Methods

Temp, °C	K, M^{-1} [a]	k_f/k_r, M^{-1} [b]	K, M^{-1} [c]
40	0.046	0.046	0.044
25	0.077	0.075	0.086
12	0.13	0.11	0.14
0	0.21	0.18	0.23

[a] Fast exchange data (ω_{mean}). [b] Slow exchange data. [c] Values interpolated from Table I.

The kinetics of formation and dissociation of 2-hydroxy-2-hydroperoxypropane present similar characteristics to those of other hydrogen peroxide additions to carbonyl compounds.[12,13] The mechanisms for concerted general acid and base catalysis proposed by Jencks[12,13] seem to fit our kinetic results without modification.

The kinetic results obtained by both uv and nmr line-broadening techniques are summarized in Figure 1. As can be seen the agreement among the data is quite good considering the variable reactant concentrations in the two types of experiments. From the rate profile of Figure 1, it would seem possible to study the kinetics of the reaction by the nmr line-broadening technique at pH values lower than 2, since the reaction

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(11) G. Socrates, *J. Org. Chem.*, **34**, 2958 (1969).

(12) E. G. Sander and W. P. Jencks, *J. Amer. Chem. Soc.*, **90**, 4377 (1968).

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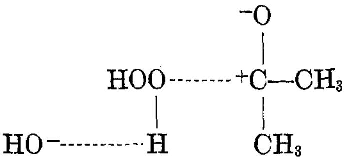
is also fast in this region. However, this is not possible since the formation of 2,2-bis(hydroperoxy)propane (reaction 3) is acid-catalyzed and becomes very important in acid solutions. In the range of concentrations used in the uv technique (dilute solutions) this secondary reaction is not significant due to the high water concentrations involved in this type of experiment. Further, it was observed that there is no important reaction at basic pH other than the formation of 2-hydroxy-2-hydroperoxypropane. This fact immediately suggests one of the conditions under which isolation of this compound might be possible, that is, in the basic solutions of acetone and hydrogen peroxide.

The activation parameters obtained for the base-catalyzed reaction between acetone and hydrogen peroxide support the proposed mechanism. The similarity of the entropy of activation of the forward reaction $\Delta S_f^{\ddagger}$ with the entropy of the reaction ΔS ($\Delta S_f^{\ddagger} = -18$ cal mol^{-1} deg^{-1} and $\Delta S = -28$ cal mol^{-1} deg^{-1}) suggests that the transition state closely resembles the products and that a termolecular interaction among the hydrogen peroxide, the general base (OH^- in this case), and acetone is fundamental to the transition state



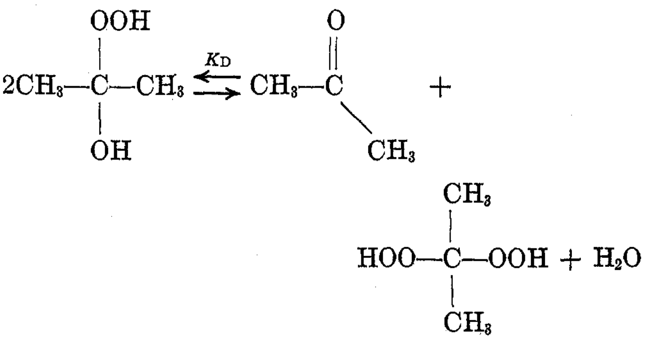
$$\mathrm{HO^{-}\cdots H{-}OO\cdots{}^{+}C(O^{-})(CH_3){-}CH_3}$$

The reaction is accompanied by a substantial loss in entropy owing to the loss in translational freedom of hydrogen peroxide. Further, the small value in activation energy agrees with the fact that the carbonyl group of acetone is highly polarized which facilitates an attack on the carbonyl carbon by a hydrogen peroxide anion.

In the reverse reaction a higher value of the activation energy would be expected since bond breaking is in process, and the positive change in entropy agrees with the dissociation process of 2-hydroxy-2-hydroperoxypropane to form two particles.

The formation of 2-hydroxy-2-hydroperoxypropane as an intermediate has been postulated in the oxidation of ketones by the Baeyer–Villiger reaction.[14,15] Under the mild conditions employed in this study, this oxidation is at most a minor side reaction. Formation of methyl acetate was detected by nmr; however, this was seen only in the more concentrated solutions that were kept at 40° for several days.

The lack of stability of adduct I in aqueous solution is a thermodynamic as well as kinetic phenomenon. This can be seen from the equilibrium constants involved in the different processes. Constants for the processes represented by eq 1 and 3 can be combined to give the disproportionation reaction



$$2\,\mathrm{CH_3{-}C(OOH)(OH){-}CH_3} \overset{K_D}{\rightleftarrows} \mathrm{CH_3{-}C(=O){-}CH_3} + \mathrm{HOO{-}C(CH_3)_2{-}OOH} + \mathrm{H_2O}$$

where

$$K_D = \frac{[\mathrm{CH_3COCH_3}][(\mathrm{CH_3})_2\mathrm{C(OOH)_2}][\mathrm{H_2O}]}{[(\mathrm{CH_3})_2\mathrm{C(OH)(OOH)}]^2}$$

From these equations, it can be seen that $K_D = K_3/K$, where K_3 is the equilibrium constant for reaction 3. The value of constant K is 0.08 M^{-1} at 25°; the value of K_3 is 170.[1a] Therefore K_D equals 2×10^3 which indicates that adduct 1 has a significant tendency to undergo disproportionation.

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