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KINETICS OF CARBOXYLIC ACID FORMATION IN THE COMBUSTION OF ALCOHOLS

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By

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FOREWORD

This work was conducted at the Belvoir Fuels and Lubricants Research Facility (SwRI), San Antonio, TX under Contract Nos. DAAK70-85-C-0007 and DAAK70-87-C-0043 during the period September 1986 through December 1987. The work was funded by the U.S. Army Belvoir Research, Development and Engineering Center, Ft. Belvoir, VA, In-House Laboratory Independent Research (ILIR) Program, ILIR Work Unit No. 521. Mr. F.W. Shaekel (STRBE-VF) served as the contracting officer's representative and Mr. M.E. LePera (STRBE-VF) as the project technical monitor.

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I. INTRODUCTION

Throughout the history of combustion chemistry, several stable intermediates and free radical species have been discovered. Lewis and von Elbe ($\underline{1}$)* give some mention of formic acid (HCOOH), but, for the most part, the formation of carboxylic acids (RCOOH) has been ignored in the combustion chemistry of alcohols and hydrocarbons. This lack of study is because combustion science has placed major emphasis on the kinetics of high-temperature (500 to 2000K) oxidation reactions. Carboxylic acids are not observed in the high-temperature oxidation of alcohols and hydrocarbons because: (1) they are relatively unstable oxidation products, and (2) their precursors may be either unstable or decompose into other products. As of late, the presence of carboxylic acids in low-temperature (<500K) combustion environments has become more important because of the role that the carboxylic acids play in the corrosion of rings and cylinder bores of alcohol-fueled spark-ignition engines.($\underline{2}$-$\underline{15}$) Recent work ($\underline{7}$,$\underline{11}$,$\underline{12}$) has shown that, in addition to carboxylic acids, peroxides are formed in the combustion of alcohols. Peroxides significantly increase the corrosion rate by increasing the rate of metal oxidation. In methanol-fueled engines, a peroxide known as methylenehydroxyperoxide, CH_2OH-O-O-CH_2OH, appears to significantly enhance the corrosive effect of formic acid.

In this report, the kinetics and thermodynamics of formation of carboxylic acids and methylenehydroxyperoxide derivatives formed by the reaction of hydrogen peroxide with aldehydes are examined. Based on earlier work ($\underline{16}$,$\underline{17}$), the reaction of hydrogen peroxide with aldehydes appears to be the main source of carboxylic acid and organic peroxide formation in alcohol combustion.

II. BACKGROUND

A. Engine Wear Studies

Investigations involving laboratory test engines ($\underline{2}$-$\underline{5}$) and vehicle fleets ($\underline{6}$) have shown that the use of neat methanol in spark-ignition engines can cause unusually high levels of wear during conditions of warm-up and cold-weather operation. Test results from

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* Underscored numbers in parentheses refer to the List of References at the end of this report.

engines, including a 350-CID V8, a 2.3-liter 4-cylinder, and a single-cylinder CLR, show that increased wear principally occurs in the upper-cylinder bore and ring areas. Surface profiles and electron micrographs of the cylinder bore and ring areas indicate that corrosion plays a significant role in this wear mechanism.

Laboratory-scale engine tests showed that the wear rate was strongly dependent on the temperature of the oil and coolant, increasing exponentially as the temperature was decreased. Test engines fueled with methanol and ethanol each containing 11-percent water experienced dramatically higher wear rates than those fueled with neat alcohols. These effects of temperature and water suggested that the cylinder walls contained a liquid fuel layer that could provide a relatively cool medium for corrosive combustion products to dissolve. Comparison of the wear rate data with a simple model (7) for the evaporation of a liquid layer showed that both processes had similar temperature dependencies. The evaporation model was based on the theory that as long as liquid fuel was on the cylinder wall, deleterious combustion products could dissolve in the fuel, leaving a corrosive residue on the metal surface. It was assumed that the oil film was either diluted or washed off the upper-cylinder wall by liquid methanol trapped in the crevice bound by the piston, ring, and cylinder wall. Schwartz (8) proposes that methanol readily forms an emulsion with the relatively cool lubricant being deposited on the cylinder bore. When the combustion process heats up the cylinder wall surface, the methanol evaporates, forming vapor bubbles that burst and form holes in the oil film. This is a possible mechanism for exposing the metal surface to corrosive combustion products.

Basically, three possible corrosion mechanisms have been proposed. Fuel impurities, such as chlorine, are known to cause corrosion in methanol-fueled engines.(9) Chlorinated hydrocarbon contaminants in the fuel are converted to hydrochloric acid in the combustion process. The hydrochloric acid enhances the corrosive wear in the engine; however, removing all traces of chlorine from the fuel did not eliminate the wear problem. In a second attempt to explain the corrosion, it was proposed (10) that nitric acid plays an important role in the corrosion mechanism since oxides of nitrogen are formed by combustion. However, an evaluation of engine wear with methanol fuel carried out in a nitrogen-free atmosphere has shown that oxides of nitrogen have no effect on wear.(7) The third and prevailing theory is that the corrosive wear is caused by the products of the combustion of methanol.(11-15)

Combustion residues (12) consisting of water, methanol, formaldehyde, acetaldehyde, formic acid, acetic acid, and methylenehydroxyperoxide were found to be formed by the combustion of alcohol pools and liquid layers. Alcohol pools burned in a cast iron vessel caused considerable corrosion while those burned in aluminum and stainless steel vessels did not cause any corrosion of the metal. In the cast iron container, the formic acid and peroxide reacted with the metal to form iron formate. Analysis of the corrosion product indicated that its empirical formula was $FeO(HCOO)H_2O$. The results of several experiments showed that the important combustion intermediates that cause corrosion of cast iron are formic acid and methylenehydroxyperoxide, a peroxide formed by the reaction of hydrogen peroxide with formaldehyde.

In burning methanol pools and liquid layers, the combustion intermediates, including water, formaldehyde, formic acid, and hydrogen peroxide diffuse from the gas phase to the liquid surface and dissolve. The propensity for these polar intermediates to dissolve in methanol is much higher than hydrocarbon fuels because methanol is also a very polar compound. It is believed that this is the basis for the corrosion of rings and cylinder bores in methanol-fueled spark-ignition engines. Excessive cylinder bore and ring wear have also been observed in gasoline-fueled engines when liner temperatures are extremely low ($< 30°C$).(8) In this case, the condensation of water on the cylinder wall and the subsequent dissolution of corrosive combustion intermediates appear to be the cause.

B.   Combustion Kinetics

In reviewing the literature, it is apparent that the mechanism for the formation of formic acid in the combustion of alcohols and hydrocarbons is not well known. About forty years ago, Bone and Gardner (16) and Style and Summers (17) studied the slow gas phase oxidation chemistry of methane, methanol, and formaldehyde at temperatures in the range of 100° to 300°C. This temperature range is of particular interest because it is what one might expect to find near the surface of a burning liquid pool or cold wall. In their studies of the low-temperature oxidation of formaldehyde, they found several combustion intermediates, including formic acid, performic acid, and what appeared to be methylenehydroxyperoxide. These intermediates were also observed in the low-temperature oxidation of methanol, and it was apparent that their formation rates were proportional to the concentration of formaldehyde that has been detected in the pyrolysis (18) and oxidation (19) of methanol. The results of the formaldehyde oxidation

work ([16,17](#)) indicated that methylenehydroxyperoxide, $CH_2OH-O-O-CH_2OH$, was a precursor to the formation of formic acid and performic acid hydrogen, which could not, otherwise, be accounted for. Methylenedydroxyperoxide appears to be formed by the reaction of hydrogen peroxide with formaldehyde as follows:

$$H_2O_2 + 2HCHO = \overset{\overset{\displaystyle OH}{|}}{CH_2}-OO-\overset{\overset{\displaystyle OH}{|}}{CH_2} \qquad (1)$$
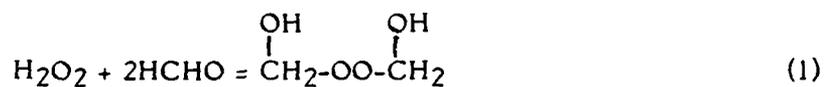
and it is believed to decompose via

$$\overset{\overset{\displaystyle OH}{|}}{CH_2}-OO-\overset{\overset{\displaystyle OH}{|}}{CH_2} = 2HCOOH + H_2 \qquad (2)$$
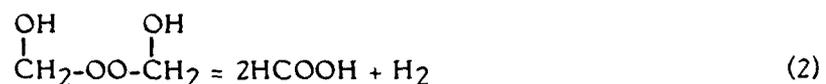
forming hydrogen and two moles of formic acid. The mechanism for the formation of methylenehydroxyperoxide in the combustion of methanol and formaldehyde is not known, but it is highly probable that the species involved are hydrogen peroxide and formaldehyde. It is well known ([1,19](#)) that hydrogen peroxide is formed as an intermediate in the combustion of alcohols and hydrocarbons. It is especially abundant in the oxidations of methanol and formaldehyde because free radical reactions, such as

$$CH_2OH + O_2 = HCHO + HO_2 \qquad (3)$$

and

$$HCO + O_2 = CO + HO_2 \qquad (4)$$

followed by

$$HO_2 + RH = H_2O_2 + R \qquad (5)$$
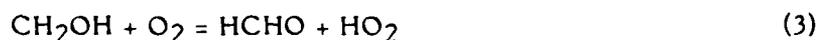
occur very frequently. Formic acid is not observed in the high-temperature oxidations of methanol and formaldehyde.([19](#)). This may be due to the fact that peroxides are relatively unstable at temperatures greater than 500K. If hydrogen peroxide decomposes via

$$H_2O_2 = 2OH \tag{6}$$

it would not have an opportunity to react with formaldehyde to form methylene-hydroxyperoxide, which would probably be even more unstable at high temperatures. This may well be the reason that formic acid is found only in low-temperature combustion, i.e., in regions of flame quench, such as the gaseous boundary layer of a cylinder wall where the intermediate, methylenehydroxyperoxide, could possibly exist.

Recent work by Sarkissian and Malkhassian (20) on the mass spectrometric analysis of the oxidation products of formaldehyde showed that several intermediates, including formic acid and hydrogen peroxide were formed, but performic acid and methylenehydroxyperoxide were not detected in the gas phase. If methylenehydroxyperoxide had been an important intermediate in the formation of formic acid, its steady-state concentration must have been very low. The oxidation experiments were carried out at relatively high temperatures ranging from 350° to $500^\circ C$. At these temperatures, methylenehydroxyperoxide is, no doubt, very unstable, and its concentration would be too low to allow detection.

The kinetics of the reaction of hydrogen peroxide with formaldehyde in the aqueous phase was recently studied by Nikolaev and Ignatov (21), Baranchik, et al. (22) in the temperature range of 20° to $60^\circ C$. They concluded that hydrogen peroxide disappears via

$$2H_2O_2 = O_2 + 2H_2O \tag{7}$$

and

$$H_2O_2 + HCHO = HCOOH + H_2O \tag{8}$$
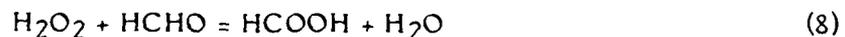
forming a small amount of oxygen and formic acid as the main product. The decomposition of hydrogen peroxide in Reaction 7 is relatively slow compared to Reaction 8 involving formaldehyde. This mechanism put forth by Baranchik, et al. assumes that only one mole of formic acid is formed from one mole of hydrogen peroxide, and there is no evidence given in their paper for the formation of a methylenehydroxyperoxide intermediate. If methylenehydroxyperoxide was actually

present in the aqueous solutions containing hydrogen peroxide and formaldehyde as perceived by Fenton (23) several decades ago, its decomposition would most probably lead to the formation of two moles of formic acid for each mole of hydrogen peroxide consumed.

III. OBJECTIVE

The purpose of this work was to determine the mechanism of formation of carboxylic acids and methylenehydroxyperoxide-type derivations that are found in residues resulting from the low-temperature combustion of alcohols. The kinetics of the hydrogen peroxide/formaldehyde reaction were examined because this system appeared to be the most favorable candidate, based on the reactive stable intermediates previously detected in the combustion of methanol. The objective has been extended to include analogous reactions of hydrogen peroxide with deuterated formaldehyde (DCDO), acetaldehyde (CH_3CHO), and chloral (CCl_3CHO). The purpose of extending the kinetics study to these aldehydes was twofold; (1) to establish a more comprehensive mechanism for the reaction of hydrogen peroxide with aldehydes, and (2) to determine the importance of this reaction in forming higher molecular weight carboxylic acids in the combustion of the higher alcohols. Ultimately, the specific rate constants and thermodynamic properties of reaction intermediates, etc., determined from this low-temperature study of hydrogen peroxide/aldehyde reactions in the aqueous phase, will be of value in evaluating the significance of these reactions in the low-temperature combustion of alcohols.

IV. EXPERIMENTAL

A. Experimental Procedures

The kinetics of the reactions of hydrogen peroxide with aldehydes were as examined in aqueous solutions containing high concentrations of the aldehyde and relatively low concentrations of hydrogen peroxide. Initial concentrations of HCHO and DCDO ranged from 0.05 to 1.0 moles/liter, and the initial H_2O_2 concentration ranged from 0.015 to 0.019 moles/liter. Initial concentration of CH_3CHO ranged from 0.35 to 3.30 moles/liter

and that of H_2O_2 was 0.112 moles/liter. The initial concentration of CCl_3CHO ranged from 0.21 to 2.02 moles/liter and that for H_2O_2 was 0.028 moles/liter.

1. Reagents

Research grade paraformaldehyde and acetaldehyde and USP grade chloral hydrate were used in this study. Deuterated paraformaldehyde with a purity greater than 99.6 percent based on its deuterium content was also obtained. Formaldehyde solutions were prepared by refluxing paraformaldehyde in distilled water for at least 2 hours. Solutions of acetaldehyde and chloral were prepared by simply mixing acetaldehyde and chloral hydrate with water.

2. Apparatus

The reactions were carried out in 250-mL polypropylene volumetric flasks that were placed in a constant temperature $\pm$ 0.2°C water bath. Hydrogen peroxide concentrations were monitored throughout the course of the reaction, and the carboxylic acid, e.g., formic acid, concentration was measured after most of the peroxide was consumed. Since the aldehyde concentration was, in most cases, several times higher than the hydrogen peroxide concentration, its concentration was assumed to be essentially constant.

Reactions of hydrogen peroxide with aldehydes were slow, taking from 3 hours to several days, depending on the temperature. However, when mixing high concentrations of hydrogen peroxide with formaldehyde at room temperature, there was a temperature rise within 30 minutes that indicated the formation of a reaction intermediate. The heat of this reaction was measured in a small Dewar flask equipped with a thermometer and a large rubber stopper. The heat of reaction was determined from the temperature rise and the concentrations of hydrogen peroxide and formaldehyde.

3. Analytical Methods

The peroxides were determined spectrophotometrically by the method of Egerton, et al. (24) using titanous chloride reagent. Peroxides produce a yellow coloring that absorbs at 410 nm. The method is particularly suited for measuring hydrogen peroxide in aqueous

solutions. Egerton, et al. pointed out that there could be some problem in analyzing peroxides when formaldehyde was present because formaldehyde peroxide is formed. The so-called formaldehyde peroxide, better named methylenehydroxyperoxide, was observed by Bone and Gardner (16) in the low-temperature oxidation of formaldehyde. Bone and Gardner also observed performic acid in the products of formaldehyde oxidation. In their analysis, methylenehydroxyperoxide was found to be decomposed with caustic alkali with evolution of hydrogen; it liberated iodine from potassium iodide very slowly and incompletely. Contrarily, performic acid was not so decomposed and liberated iodine rapidly. The titanous chloride method was tested on aqueous solutions of hydrogen peroxide and similar solutions containing formaldehyde and formic acid. For the pure hydrogen peroxide solutions and solutions containing formic acid, the color developed immediately. In solutions containing low concentrations (≈ 0.1 moles/liter) of formaldehyde, the color developed slowly, taking about 30 minutes before the optical density at 410 nm reached the same value obtained with the formaldehyde-free sample. It was found that peroxide contents of samples containing aldehydes could be determined if the aldehyde concentrations were sufficiently dilute and ample time (30 minutes) was allowed for the color to develop.

In practice, a 1-mL aliquot of the peroxide/aldehyde reactant mixture was diluted with 24 mL of H_2O in a 25-mL volumetric flask. To 3 mL of this solution, 1 mL of titanous chloride reagent was added, and the contents were placed in a spectrophotometric cell. After 30 minutes, the optical density at 410 nm was measured using a reference cell containing 1 mL of titanous chloride reagent and 3 mL of distilled water. The titanous chloride reagent was prepared as specified by Egerton, et al.(24).

This procedure was used to analyze the samples from reactions of H_2O_2 with formaldehyde, HCHO and DCDO, and chloral, CCl_3CHO. While performing experiments with acetaldehyde, CH_3CHO, it was found that relatively high concentrations of aldehyde were required in order to achieve a significant reaction rate. As a result, it was necessary to dilute the 1-mL reaction mixture sample with 99 mL of H_2O. To compensate for the four-fold increase in dilution, the initial H_2O_2 concentration used in the H_2O_2/CH_3CHO reaction was increased by a factor of four to 0.112 moles/liter.

Formaldehyde was determined by the spectrophotometric method of Bricker and Johnson (25) using chromotropic acid reagent, and the "alkali peroxide method."(26) A spectrophotometer was used to measure the peroxide and formaldehyde concentrations.

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Ion chromatography (27) was used to determine the concentrations of formate and acetate ions. The term ion chromatography describes the analysis of dissolved ions by ion exchange chromatography using an electrical conductivity detector. The ion chromatograph was particularly useful in analyzing solutions containing more than one ion, e.g., both formate and acetate ions were found in the products of the H_2O_2/CH_3CHO reaction. The formations of formic, acetic, and trichloroacetic acids were also determined by titration with KOH solution. This analysis was done at the end of each run after most of the peroxide was consumed. These measurements were used to compute the number of moles of acid formed per mole of peroxide consumed in the reaction.

A gas chromatograph equipped with a thermoconductivity detector, temperature programming, and a glass chromosorb 107 column was used to analyze the gases H_2, CH_4, and traces of O_2 and CO_2 that were evolved in the reaction of hydrogen peroxide with aldehydes.

In the reaction of hydrogen peroxide with deuterated formaldehyde (DCDO), an analytical procedure was developed to determine if deuterium gas was evolved in the reaction. To discern between H_2 and D_2, mass spectrometry appeared to be the most appropriate method of analysis. However, this was not a straight forward procedure because the available mass spectrometers were capable of only analyzing species with masses greater than 10 mass units. To resolve this problem, the gas evolved in the $H_2O_2/DCDO$ reaction was passed over copper oxide at about 300°C and converted to water. The heavy water, D_2O, formed by the oxidation was then analysed by a gas chromatograph interfaced with a mass spectrometer.

B.   Results

1. $H_2O_2/HCHO$ Reaction

The kinetics of the reaction of hydrogen peroxide with formaldehyde was examined in aqueous solution over the temperature range of 23° to 70°C. The rate of this reaction was found to be first order in the concentration of peroxide and of complex order in the formaldehyde concentration. Fig. 1 shows the typical first-order decay in the concentration of peroxide at different concentrations of formaldehyde. Note the peroxide
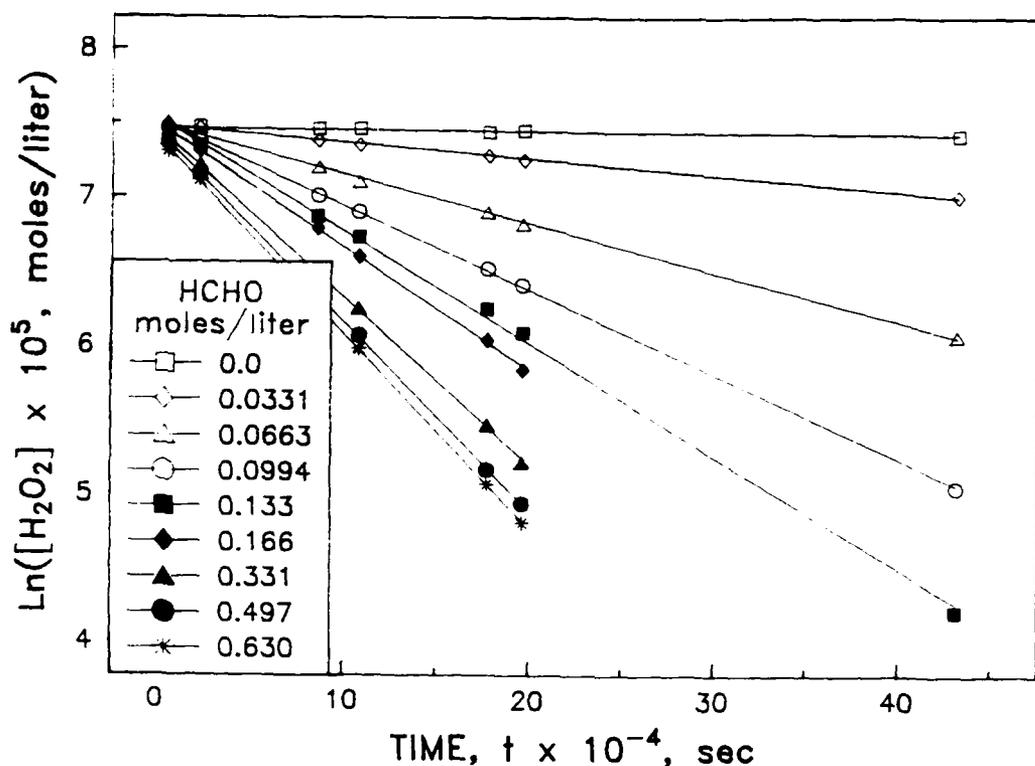
Figure 1. The first order decay of peroxide in formaldehyde solutions at 23.5°C

concentration in these experiments should be thought of as the sum of the concentrations of hydrogen peroxide, methylenehydroxyperoxide, and performic acid, which no doubt forms to some extent by the reaction of hydrogen peroxide with formic acid. Basically, the slopes of the curves shown in Fig. 1 indicate first order decay constants, k(HCHO), for the disappearance of total peroxide at different concentrations of formaldehyde. Fig. 2 shows the effect of formaldehyde concentration on rate constant, k(HCHO), for total peroxide decay. It is seen that k(HCHO) first increases dramatically with increasing formaldehyde concentration, and then gradually approaches a relatively constant (asymptotic) value that is essentially independent of aldehyde concentration. Measurements based on formic acid yield and the hydrogen peroxide consumption showed that two moles of acid were formed for each mole of peroxide consumed. This consumption was found to be true throughout the formaldehyde concentration range and temperature range (23° to 70°C) over which the reaction was examined. It was also found that hydrogen and traces (ca. 1 percent) of oxygen and CO_2 gases were evolved in the reaction, but these were not determined quantitatively.
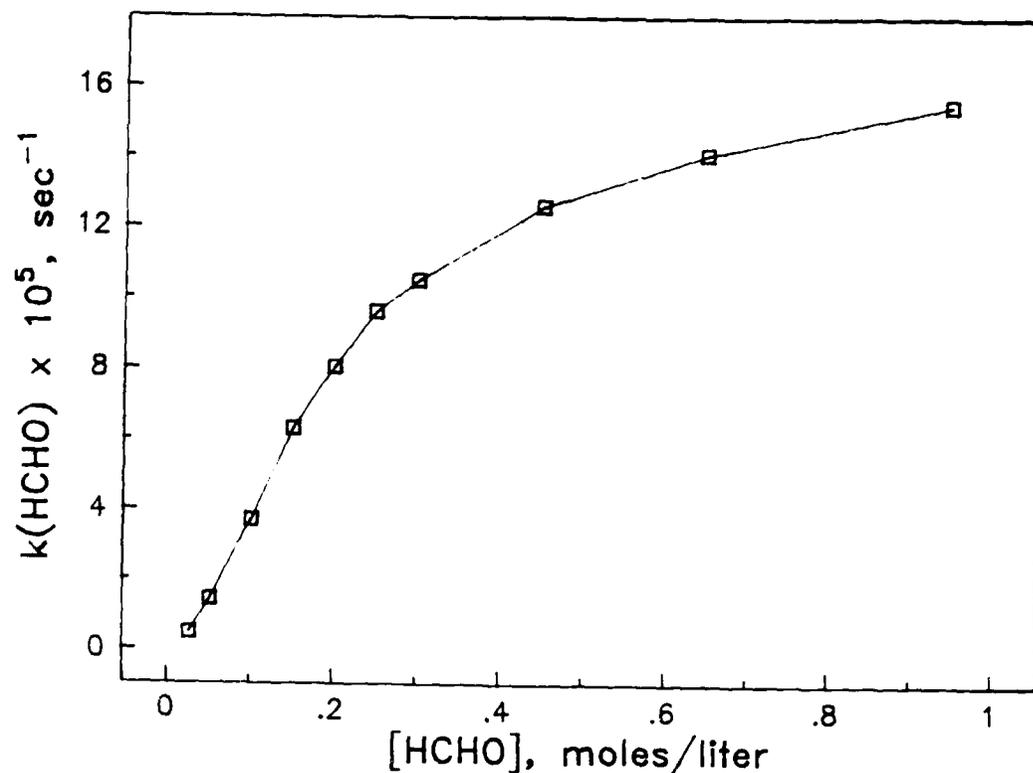
Figure 2. The effect of formaldehyde concentration on the rate constant, k(HCHO), for peroxide decay at 54.9°C

In experiments with concentrated hydrogen peroxide (30 percent) and formylin solution (37.5-percent HCHO), it was found that a significant heat release occurred within 30 minutes when these reagents were mixed. The temperature rise in the solution was too high to be attributed to a heat of mixing and, thus, was indicative of a chemical reaction. However, measurements showed that the peroxide concentration was essentially unchanged and no acid was formed after the 30-minute period. Fig. 3 shows the temperature rise versus time curve for a fairly concentrated aqueous solution of hydrogen peroxide and formaldehyde. Even though peroxide did not appear to be consumed, there was a reaction. This reaction was fast and essentially completed well before any decay in the concentration of perioxide was observed. Based on the temperature rise and the hydrogen peroxide concentration, a heat of reaction of approximately 7.9 kcal/mole of peroxide was obtained. This was found to be reasonably constant in solutions that contained at least twice as many moles of formaldehyde as peroxide. The results of these experiments suggest that a reaction intermediate, most probably methylenehydroxyperoxide, is formed by the combination of hydrogen peroxide with formaldehyde.
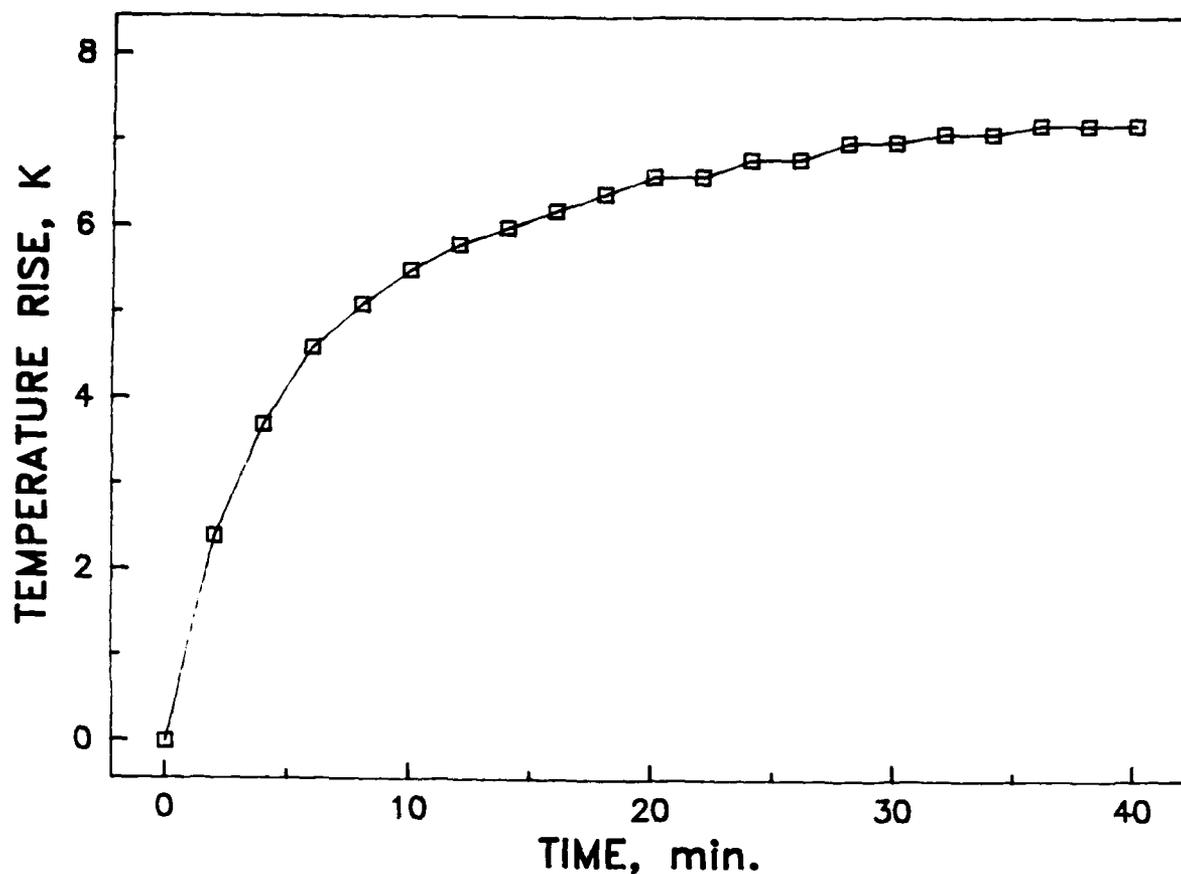
Figure 3. The initial temperature rise observed in the reaction of hydrogen peroxide with formaldehyde in aqueous solution (The concentrations were (H_2O_2) = 0.92 moles/liter and $(HCHO)$ = 7.58 moles/liter)

2. H_2O_2/DCDO Reaction

The reaction of hydrogen peroxide with deuterated formaldehyde (DCDO) was basically the same as that with HCHO except that the rate of the reaction was about an order of magnitude slower. The rate of peroxide disappearance was measured at four temperatures (40°, 50°, 60°, and 70°C) over a broad range of DCDO concentrations. In two of the runs, the peroxide decay rates were measured at constant temperature in equimolar concentrations of HCHO and DCDO, i.e., the rates in five HCHO concentrations were compared with those in five equimolar DCDO concentrations. The rate of peroxide disappearance and the dependence of the rate constant, k(DCDO), on the DCDO concentration were similar to those shown in Figs. 1 and 2 for HCHO. That is, the rate of peroxide disappearance was first order in the peroxide concentration and the rate constant for peroxide decay had a complex dependence on the DCDO concentration.

Also, analysis of the deuterated formic acid and H_2O_2 showed that two moles of acid were formed from each mole of H_2O_2 consumed. As mentioned earlier, the gas evolved from the reaction was passed over hot (>500°C) copper oxide to convert the possible products, H_2 and D_2 to H_2O and D_2O. The water formed in this procedure was analyzed by GC mass spectroscopy and found to consist mainly of D_2O. This result showed conclusively that the hydrogen evolved in the reaction of H_2O_2 with aldehydes is derived from the aldehyde.

3. H_2O_2/CH_3CHO Reaction

Acetaldehyde is an abundant intermediate in the combustion of ethanol, and it would seem that combustion residues formed in combustion engines would contain high concentrations of acetic acid. In the course of this work, combustion residues of ethanol have been analyzed for acetaldehyde and acetic acid. High concentrations of both formaldehyde and acetaldehyde were formed, but the concentration of acetic acid was very low compared to that of formic acid. This indicated that the reaction producing acetic acid is much slower than that which forms formic acid.

Measurements of the rate of the H_2O_2/CH_3CHO reaction were made at three temperatures, approximately 40°, 50°, and 60°C. At each of these temperatures, the rate of peroxide disappearance was measured over a wide range of acetaldehyde concentrations. It was found that the rate of peroxide disappearance was first order in the peroxide concentration. This result was basically the same as that shown in Fig. 1 for formaldehyde. Compared to the $H_2O_2/HCHO$ reaction, the H_2O_2/CH_3CHO reaction was more than an order of magnitude slower, and relatively high concentrations of acetaldehyde were required to increase the reaction rate to a level at which it could be measured in a reasonable time period. Figs. 4 and 5 show the dependence of the rate constant, $k(CH_3CHO)$, for peroxide decay rate on the acetaldehyde concentration. The results show that $k(CH_3CHO)$ is not as strongly dependent on acetaldehyde concentration as it is in the case of formaldehyde (see Fig. 2). Similar to the $H_2O_2/HCHO$ reaction, however, the rate constant tends to approach a constant value as the CH_3CHO concentration is increased.

Analysis of the reaction products for acetate ion and formate ion showed that acetic acid was the major product with relatively lower concentrations of formic acid.
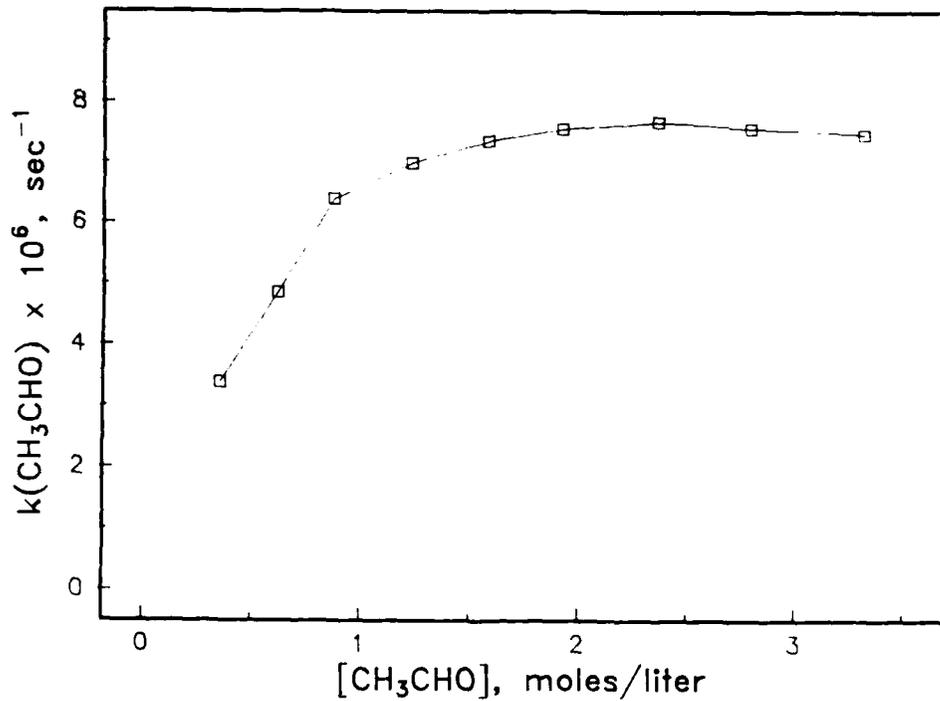
**Figure 4.** The effect of acetaldehyde concentration on the rate constant, $k(CH_3CHO)$, for peroxide decay at 40°C
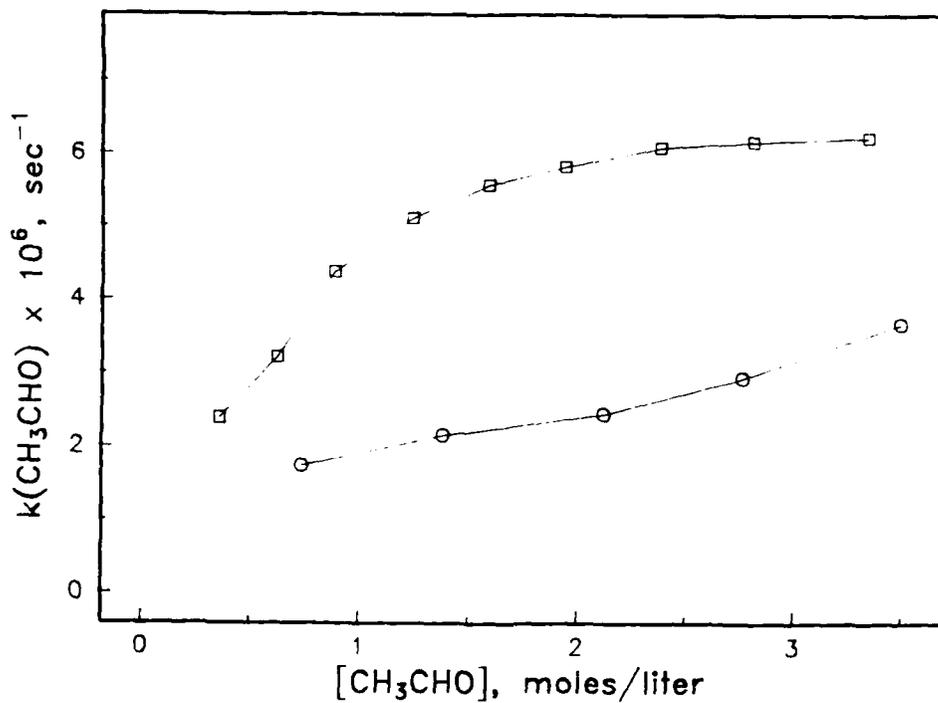
Figure 5. The effect of acetaldehyde concentration on the rate constant, $k(CH_3CHO)$, for peroxide decay at 49.3° and 59.6°C
(○ - 49.3°C; □ - 59.6°C)

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Titration of the reaction products with KOH showed that the amount of acid formed for each mole of peroxide consumed varied from 1.35 to about 2.18 moles. The molecularity of the reaction did not appear to correlate with the reaction temperature; the ratio was 1.35 at 40°C, 2.18 at 50°C, and 1.64 at 60°C. Although the ratio varied significantly with temperature and from run to run, it was relatively constant for all CH_3CHO concentrations examined in a particular run.

Gaseous products consisting of H_2 and CH_4 were formed in very low yield compared to the yield of H_2 in the $H_2O_2/HCHO$ reaction. The product mixture had an H_2/CH_4 molar ratio of about 2 to 1.

4. H_2O_2/CCl_3CHO Reaction

As a sequel to the H_2O_2/CH_3CHO reaction, the analogous reaction with chloral, CCl_3CHO, was examined This reaction was studied in order to better understand the mechanism of the reaction of H_2O_2 with aldehydes. In contrast to the CH_3 group in acetaldehyde, the CCl_3 group has a much higher electron affinity and tends to withdraw electron density from the formyl group. This affects bond strengths, which influence the rate of chemical reaction.

The H_2O_2/CCl_3CHO reaction rate was measured in the temperature range 30° to 60°C over a broad range of chloral concentrations. The rate of disappearance of peroxide was first order in the peroxide concentration, similar to that found for formaldehyde and acetaldehyde. The rate constants, $k(CCl_3CHO)$, were derived from plots of Ln (peroxide) versus time similar to that shown in Fig. 1. The reaction of H_2O_2 with chloral was slower than that with formaldehyde, but faster than the acetaldehyde reaction. Figs. 6 and 7 show the effect of chloral concentration on the rate constant, $k(CCl_3CHO)$, for peroxide decay measured at 29.7°, 39.9°, 49.3°, and 59.1°C. The results show that the rate constant, $k(CCl_3CHO)$, increases sharply with the chloral concentration. This is in contrast to the relatively weak dependence of the rate constant, $k(CH_3CHO)$, on the concentration of acetaldehyde in the H_2O_2/CH_3CHO reaction.

An extensive analysis of the H_2O_2/CCl_3CHO reaction products was not made. It was assumed that the main reaction product was trichloroacetic acid, CCl_3COOH. The yield of acid formed per mole of peroxide consumed varied significantly with the reaction
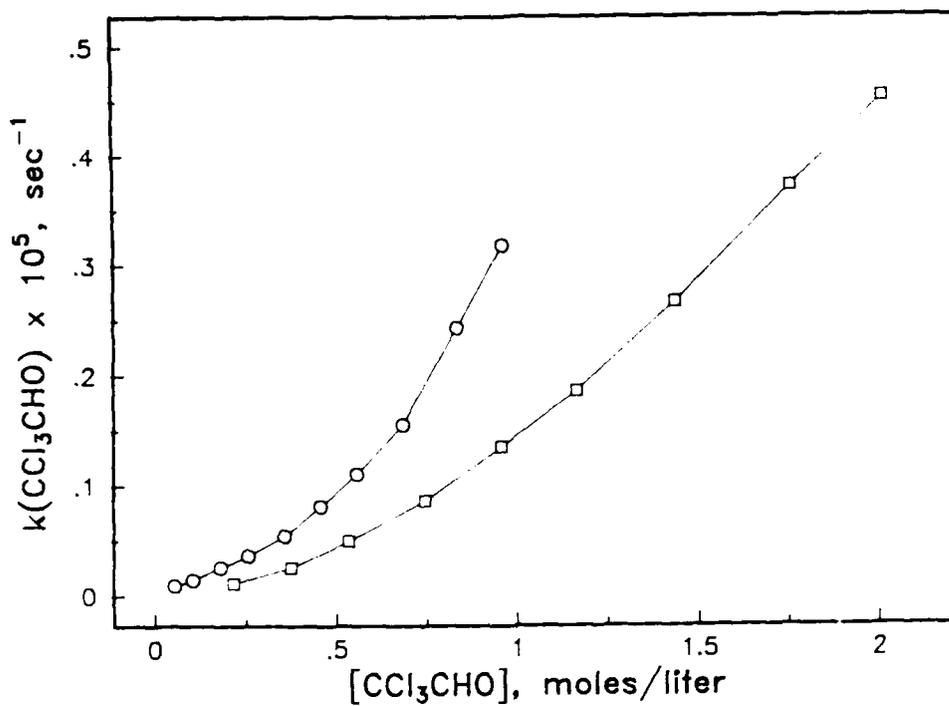
Figure 6. The effect of chloral concentration on the rate constant, k(CCl₃CHO), for peroxide decay at 29.7° and 39.3°C
(○ - 39.3°C; □ - 29.7°C)
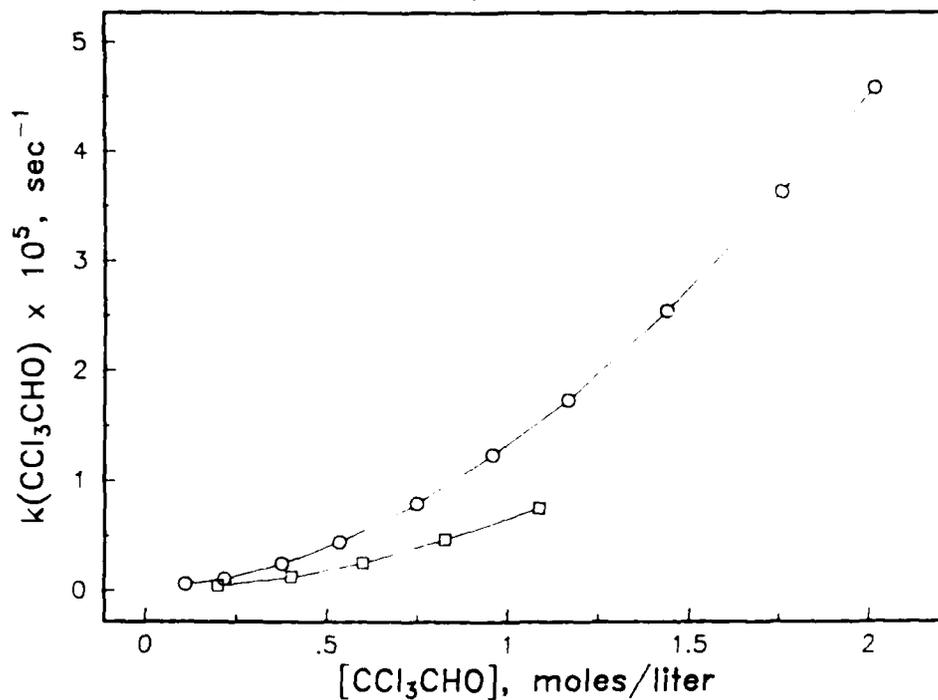
Figure 7. The effect of chloral concentration on the rate constant, k(CCl₃CHO), for peroxide decay at 49.3° and 59.1°C
(○ - 59.1°C; □ - 49.3°C)

temperature. TABLE 1 below gives the molar ratio of acid formed to peroxide consumed at different run temperature.

TABLE 1. Molar Ratio of Acid Formed to Peroxide Consumed

Reaction Temperature, $^{\circ}C$	Acid Formed/Peroxide Consumed
30	1.6
40	2.1
50	1.7
60	1.1

It is apparent from the ratios of acid formed to peroxide consumed that the temperature could have an effect on the reaction mechanism. However, it will be shown later that throughout the temperature range, 30° to $60^{\circ}C$, the rate constant, $k(CCl_3CHO)$, for peroxide decay is second order in the chloral concentration. Based on the results of the $H_2O_2/HCHO$ reaction, it is expected that the molar ratio of acid formed to peroxide consumed should be 2. The fact that it varies between 1 and 2 suggests one of two possibilities, (1) the mechanism of product formation is different than that for the formaldehyde reaction, or (2) there is considerable scatter or a possible error in the measurements of acid and peroxide. If there is an error, it is most probably in the acid concentration because these measurements are made in solutions containing very high concentrations of chloral. High chloral concentrations may interfere with the acid/base titration.

V. KINETICS

The experimental results agree for the most part, with the previous work of Bone and Gardner (16), Style and Summers (17), and Abel (28), which implies the reaction mechanism below

$$H_2O_2 + 2RCHO \underset{K_{-1}}{\overset{k_1}{\rightleftharpoons}} R-\overset{\overset{H}{|}}{\underset{\underset{OH}{|}}{C}}-O-O-\overset{\overset{H}{|}}{\underset{\underset{OH}{|}}{C}}-R \overset{k_2}{\longrightarrow} 2RCOOH + H_2 \qquad (9)$$
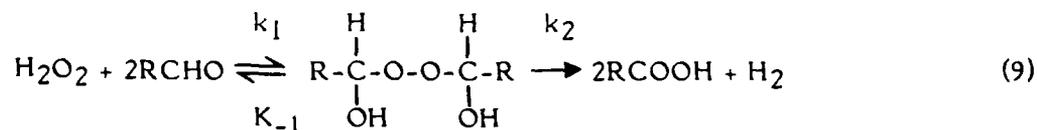
where hydrogen peroxide and aldehyde, RCHO, are in equilibrium with a derivative of methylenehydroxyperoxide; k_1 and k_{-1} are the forward and backward rate constants for the fast reaction and k_2 is the unimolecular rate constant for the irreversible decomposition of the methylenehydroxyperoxide derivative into hydrogen and the carboxylic acid, RCOOH.

This mechanism most favorably describes the kinetics of the $H_2O_2/HCHO$ reaction. In the first step, the equilibrium between hydrogen peroxide, formaldehyde, and methylenehydroxyperoxide is established. This process appears to correspond with the temperature rise that is observed in the first 30 minutes of the reaction when concentrated hydrogen peroxide and formaldehyde are mixed at room temperature. Since the rate of peroxide disappearance and subsequent formation of formic acid is relatively slow, taking several days at room temperature, it is apparent that the decomposition of methylenehydroxyperoxide is the rate-controlling step in the formation of formic acid.

To simplify the nomenclature in the mathematical analysis, the concentrations of hydrogen peroxide, aldehyde, and methylenehydroxyperoxide derivative are expressed as A, B, and C, respectively. A fourth term, P, is used to express the measured peroxide concentration; it is the sum of the hydrogen peroxide and methylenehydroxyperoxide derivative concentrations.

$$P = A + C \tag{10}$$

The equilibrium constant for methylenehydroxyperoxide derivative, C, may be expressed as

$$K_{eq} = k_1/k_{-1} = C/AB^2 \tag{11}$$

and the rate of disappearance of peroxide, P, may be expressed as

$$-dP/dt = k_2C \tag{12}$$

Note that the decomposition of hydrogen peroxide is extremely slow compared to that of the methylenehydroxyperoxide. Furthermore, most of the hydrogen peroxide is tied up with the aldehyde in the form of methylenehydroxyperoxide. Since the equilibrium

between A, B, and C is established rapidly, and the rate of decomposition of C is the rate controlling step, it can be shown that by combining Equations 10 through 12,

$$-d\ln P/dt = \frac{k_2 B^2}{1/K_{eq} + B^2} \qquad (13)$$

where $d\ln P/dt$ is the aldehyde-dependent rate constant, $k(HCHO)$, for the disappearance of peroxide, i.e., defined earlier as the slope of lines in Fig. 1. When the concentration of formaldehyde is high, e.g., $B \rightarrow \infty$, $k(HCHO) \rightarrow k_2$. Substituting $k(HCHO)$ for $d\ln P/dt$, Equation 13 may be rewritten as

$$\frac{k(HCHO)}{k_2 - k(HCHO)} = K_{eq} B^2 \qquad (14)$$

This equation may be solved iteratively by guessing values of k_2 such that the intercept of the line formed by plotting $k(HCHO)/(k_2-k(HCHO))$ versus B^2 becomes zero. This method was used in the analysis of the data on the $H_2O_2/HCHO$ and $H_2O_2/DCDO$ reactions. Fig. 8 shows a typical plot of $k(HCHO)/(k_2-k(HCHO))$ versus B^2 after the iteration is complete. This method of solving Equation 14 gives the values of both k_2 and K_{eq} derived from the rate constants for peroxide disappearance over a range of formaldehyde concentrations at a given reaction temperature. Unimolecular rate constants k_2 and the equilibrium constants K_{eq} were determined from experimental data obtained at several temperatures in the range of 23° to $70^\circ C$. Fig. 9 shows the Arrhenius plots of k_2 for the decomposition of the methylenehydroxyperoxides formed in the reactions of H_2O_2 with HCHO and DCDO. The unimolecular rate constants for the decomposition of methylenehydroxyperoxides in the HCHO and DCDO systems are

$$k_{2H} = 7.756 \times 10^{12} \exp(-25,066/RT), \; sec^{-1} \qquad (15)$$

and

$$k_{2D} = 1.408 \times 10^{12} \exp(-25,491/RT), \; sec^{-1} \qquad (16)$$

respectively.

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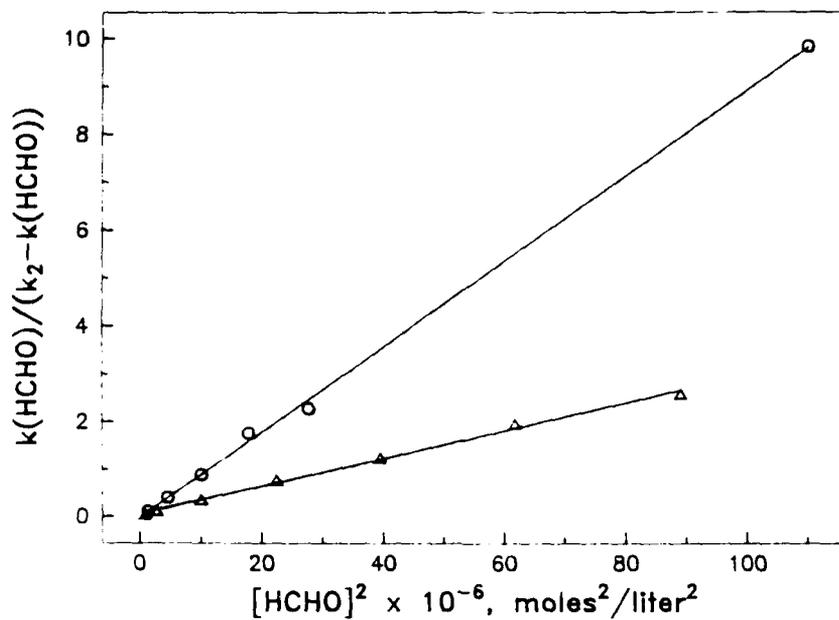
Figure 8. Correlations of the rate constant, k(HCHO), for peroxide decay with the concentration of formaldehyde
(These were derived iteratively using Equation 14 by guessing the uni-molecular rate constant, k_2 (see text). $\bigcirc$ - 23.5°C; $\triangle$ - 54.9°C)
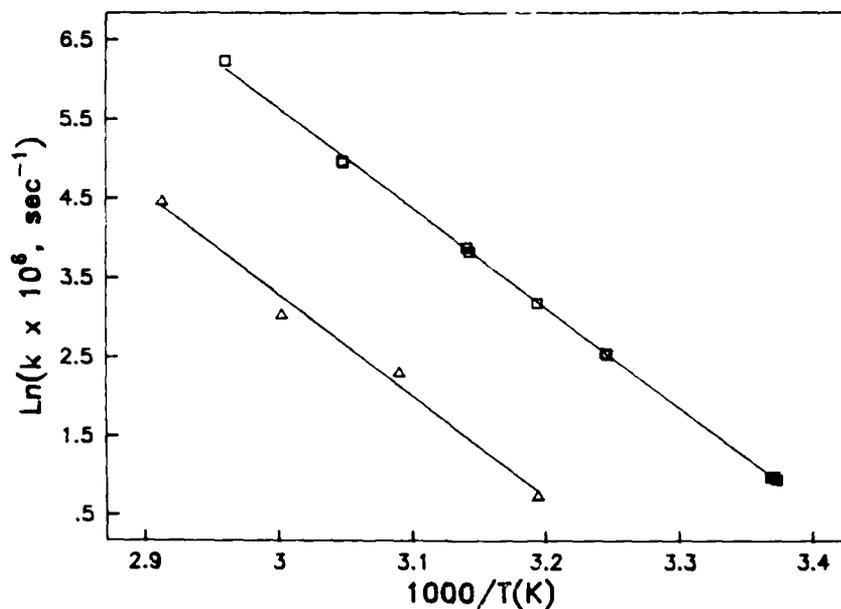
Figure 9. Arrhenius plots of the unimolecular rate constants, k_{2H} and k_{2D}, for the decomposition of the methylenehydroxyperoxide inter-mediates formed in the $\square$ - H_2O_2/HCHO and $\triangle$ - H_2O_2/DCDO reactions

In comparing k_{2H} and k_{2D}, it can be seen that they are different by about an order of magnitude over the temperature range examined. The major difference in these rate constants is found in the preexponential factors; the A_{2H}/A_{2D} ratio is about 5. The difference of 400 cal/mole in the activation energy accounts for the remaining factor of 2. In a review by Wiberg (29), it is stated that the isotope effect on the rate of chemical reactions is due principally to a decrease in the zero point energy of the chemical bonds that break during the reaction. This decrease in the rate of reaction is observed in the form of an increase in the activation energy. If it can be assumed that the rate constant expressions for k_{2H} and k_{2D} are highly accurate, it could be concluded that the difference in activation energy only accounts for about a factor of 2 in difference in rate constants. Then the alternative possibility is that the factor of 5 difference in the pre-exponential is caused by the effect of quantum tunneling. In the decomposition of methylenehydroxyperoxide, hydrogen appears to be formed by the simultaneous breaking of two C-H bonds and the formation of an H-H bond. This basically involves the transfer of two protons in the case of HCHO and two deuterium nuclei in the case of DCDO. It is conceivable that a mechanism of this type involving the transfer of protons could be affected by quantum tunneling. This is still tenuous in that only four data are available to determine the rate constant k_{2D}. An increase in the data base would substantially improve the statistical accuracy of the final expression for k_{2D}. Continued work on this problem is necessary before any definite conclusions can be made.

Fig. 10 shows the van't Hoff plot of the equilibrium constants, K_{eq}, determined for the H_2O_2/HCHO reaction. Based on a least squares fit of the data, the equilibrium constant is found to be

$$K_{eq} = 6.38 \times 10^{-5} \exp(8,425/RT), \text{ liters}^2/\text{mole}^2 \tag{17}$$

From equilibrium constant, the enthalpy and entropy may be determined for the reaction forming the methylenehydroxyperoxide intermediate. The enthalpy and entropy of the reaction are $\Delta H = -8.425$ kcal/mole and $\Delta S = -19.2$ cal/mole, respectively. The enthalpy of reaction agrees favorably with the approximate value of 7.9 kcal/mole determined by the calorimetric measurement of temperature rise in the reaction of concentrated aqueous solutions of hydrogen peroxide and formaldehyde. The agreement of these enthalpys determined independently supports the kinetic argument that the methylenehy-droxyperoxide intermediate is formed rapidly, and equilibrium is quickly established in

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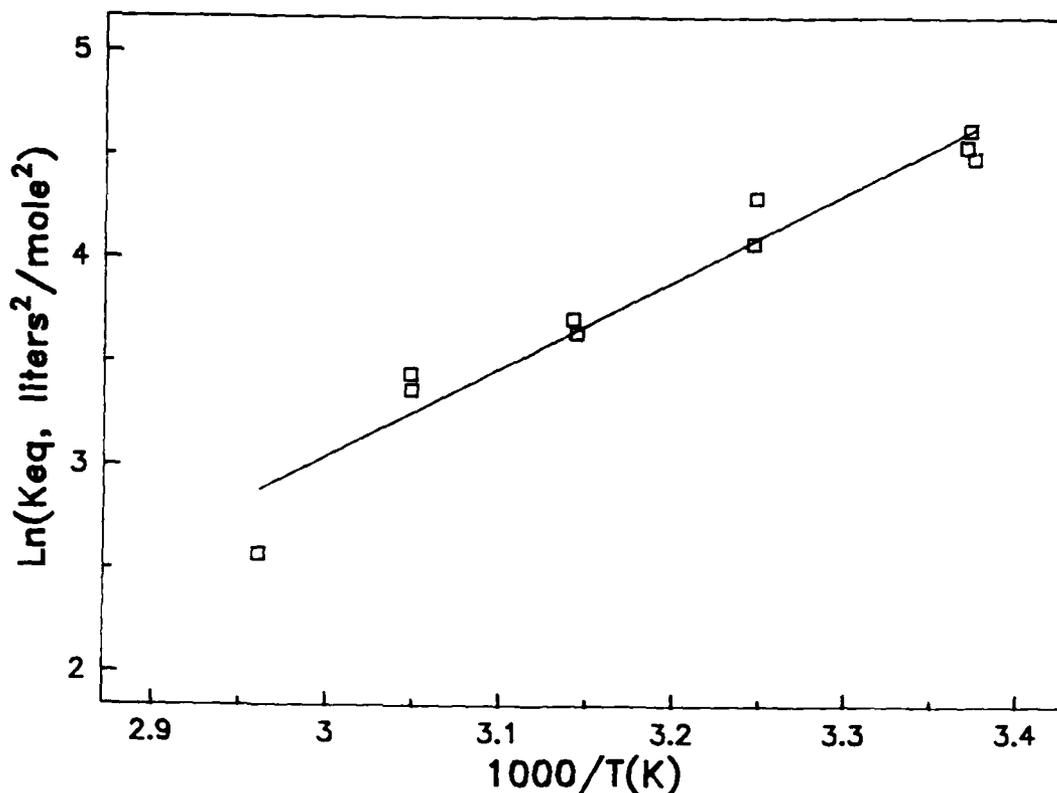
Figure 10. The van't Hoff plot of the equilibrium constant for the formation of methylenehydroxyperoxide from hydrogen peroxide and formaldehyde in aqueous solution

the H_2O_2/HCHO reaction. The negative change in the entropy of the reaction also corresponds with the associative formation of methylenehydroxyperoxide from three moles of reactants.

Fig. 11 shows the van't Hoff plot of the equilibrium constant determined for the H_2O_2/DCDO reaction. In this plot, only four data points are available, and they exhibit considerable scatter. It is expected that the slope of the line in this plot should be essentially the same as that shown in Fig. 10. The equilibrium constant derived from the data in Fig. 11 is

$$K_{eq} = 0.153 \exp (3,894/RT), \text{ liters}^2/\text{mole}^2 \tag{18}$$

and the enthalpy and entropy of reaction are $\Delta H = 3.894$ kcal/mole and $\Delta S = -3.74$ cal/mole. Although the equilibrium constants plotted in Fig. 11 are similar in magnitude to those in Fig. 10, it is very apparent that more data are required to resolve the marked
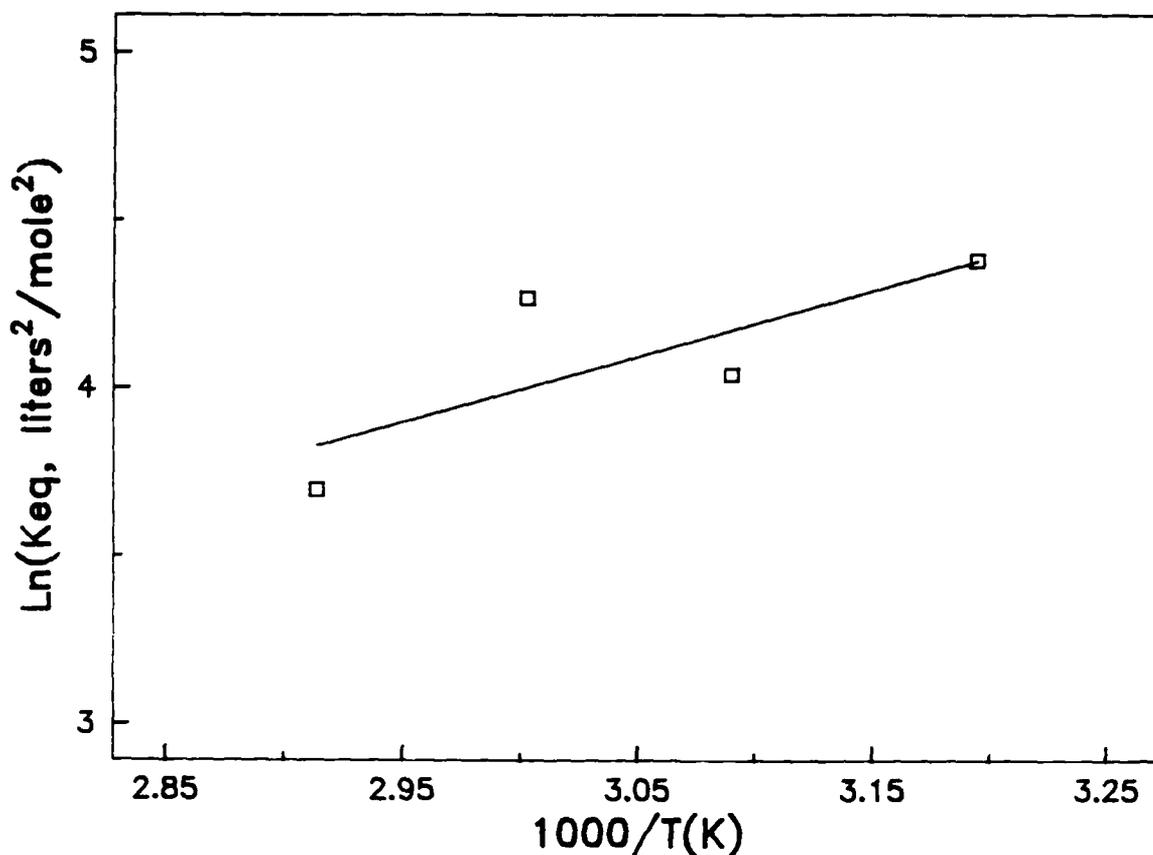
Figure 11. <u>The van't Hoff plot of the equilibrium constant for the formation of deuterated methylenehydroxyperoxide from hydrogen peroxide and deuterated formaldehyde in aqueous solution</u>

differences observed in temperature dependence and thermodynamic properties between the HCHO and DCDO systems.

The experimental results on the reaction of hydrogen peroxide with acetaldehyde are too incomplete to draw any definite conclusions. This reaction is similar to the H_2O_2/HCHO reaction in that (1) the rate of disappearance of peroxide is first order, and (2) the rate constant, $k(CH_3CHO)$, increases and then gradually approaches a constant value as the concentration of acetaldehyde is increased (see Figs. 4 and 5). At present, it is assumed that the concentration independent values of $k(CH_3CHO)$ shown in Figs. 4 and 5 are the unimolecular rate constants for the decomposition of the reaction intermediate that is assumed to be a derivative of methylenehydroxyperoxide. Fig. 12 shows an Arrhenius plot of the rate constants measured at 40°, 49.3°, and $59.6^\circ C$. The Arrhenius rate-constant expression for the rate-controlling step in the H_2O_2/CH_3CHO reaction is

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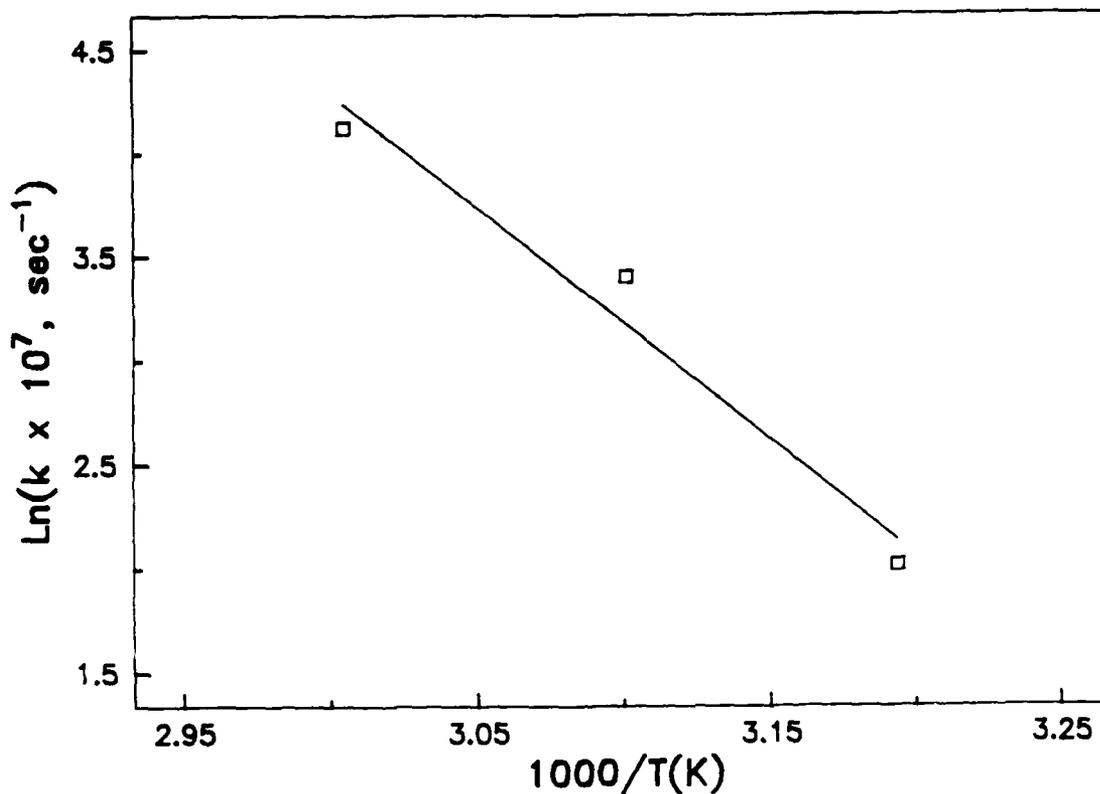
Figure 12. **Arrhenius plot of the unimolecular rate constant, k_a, for the decomposition of the intermediate in the reaction of hydrogen peroxide with acetaldehyde**

$$k_a = 2.25 \times 10^9 \exp (-22,095/RT), \sec^{-1} \qquad (19)$$

It is important to note that the actual unimolecular reaction responsible for this rate constant is uncertain. The unimolecular rate constant, k_a, could be a combination of two decomposition processes or possibly only one as in the H_2O_2/HCHO reaction. There are two reaction paths that appear to be important. In the first,

$$H_2O_2 + CH_3CHO \rightleftharpoons CH_3\text{-}\underset{\underset{H}{|}}{\overset{\overset{OH}{|}}{C}}\text{-}OOH \xrightarrow{k_a} CH_3\text{-}\underset{\underset{OH}{|}}{\overset{\overset{O}{\|}}{C}} + H_2O \qquad (20)$$
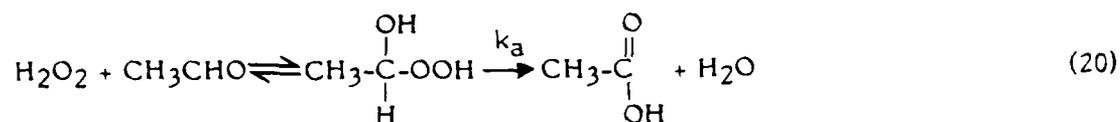
acetic acid and water are the products of the decomposition of the methylenehydroxyhydroperoxide derivative. While this reaction may be responsible for the formation of acetic acid, it does not account for the products -- formic acid, hydrogen and methane. The second reaction path

$$H_2O_2 + 2CH_3CHO \rightleftharpoons CH_3-\overset{\overset{\displaystyle OH}{|}}{C}-O-O-\overset{\overset{\displaystyle OH}{|}}{C}-CH_3 \xrightarrow{k_a} \Big\langle \begin{array}{l} 2CH_3COOH + H_2 \\ CH_3COOH + HCOOH + CH_4 \end{array} \qquad (21)$$
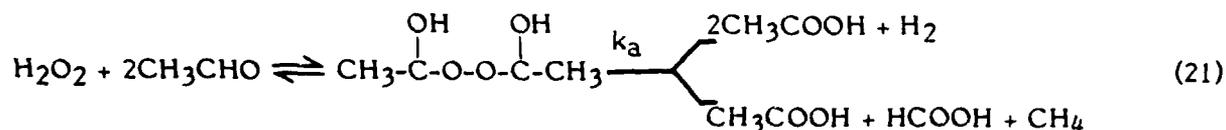
is basically the same as Reaction 9. In this mechanism, the intermediate methylenehydroxyperoxide derivative can decompose into several possible products. Qualitatively, this mechanism accounts for the observed products, formic acid, acetic acid, hydrogen, and methane. If this is the dominant reaction mechanism, the products should include two moles of carboxylic acid for each mole of peroxide consumed. The experimental results indicate that something less than two moles of acid are formed for every mole of peroxide consumed. Also, the amounts of H_2 and CH_4 were small compared to the amounts of peroxide consumed. This suggests that both reaction channels given above play a role. However, to arrive at a more definite conclusion, more effort must be made in the analysis of reaction products and the determination of the reaction mechanism.

The reaction of hydrogen peroxide with chloral was different than the reactions with formaldehyde and acetaldehyde. For the latter, the peroxide decay rate increased rapidly and then leveled off as the aldehyde concentration was increased. That type of behavior indicated that a relatively stable methylenehydroxyperoxide type intermediate was formed. The dependence of the rate constant, $k(CCl_3CHO)$, on the chloral concentration shown in Figs. 6 and 7 is very nonlinear and gives no indication that it approaches an asymptotic value that is independent of concentration. Figs. 13 and 14 show correlations of the rate constant, $k(CCl_3CHO)$, for peroxide decay with the square of the chloral concentration. The excellent correlation of $k(CCl_3CHO)$ with the square of the chloral concentration shows that the reaction is second order in the chloral concentration; the slopes of the lines in these plots are basically the rate constants for the process at the given reaction temperatures.

As mentioned previously in the experimental section of this report, the analysis of peroxide by the titanous chloride method in aqueous aldehyde solutions was complicated by the apparent formation of a methylenehydroxyperoxide intermediate. The peroxide samples for analysis had to be diluted, and a waiting period of about 30 minutes was necessary for the yellow color to develop. These precautions were absolutely imperative in the case of formaldehyde and acetaldehyde, but for chloral, the titanous chloride
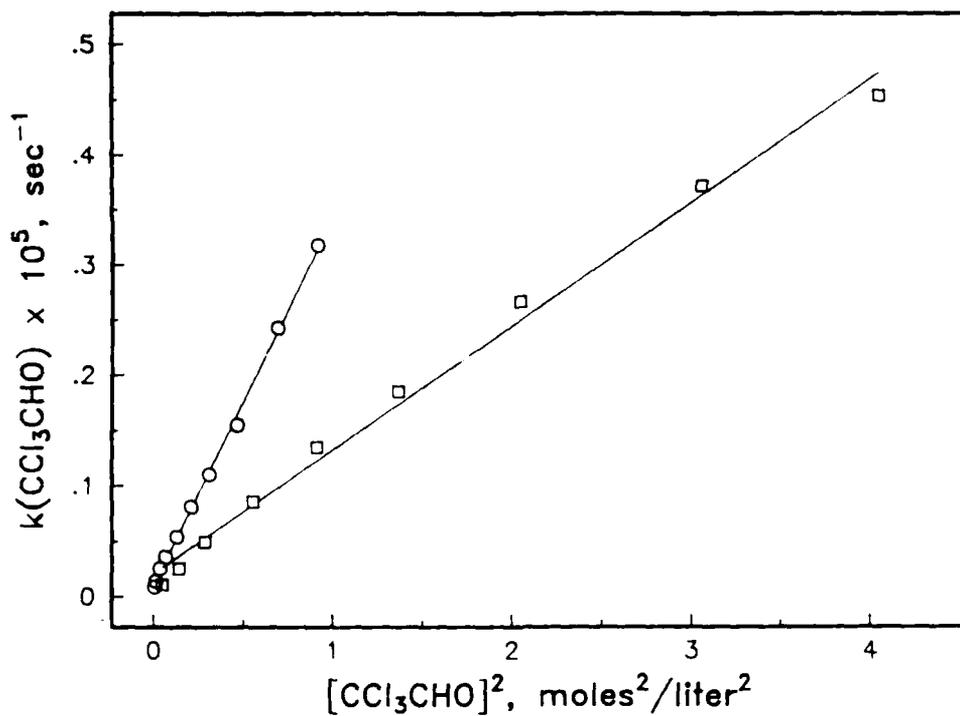
Figure 13. Correlation of the rate constant, k(CCl₃CHO), for peroxide decay with the square of the chloral concentration at 29.7° and 39.9°C
(○- 39.9°C; □- 29.7°C)
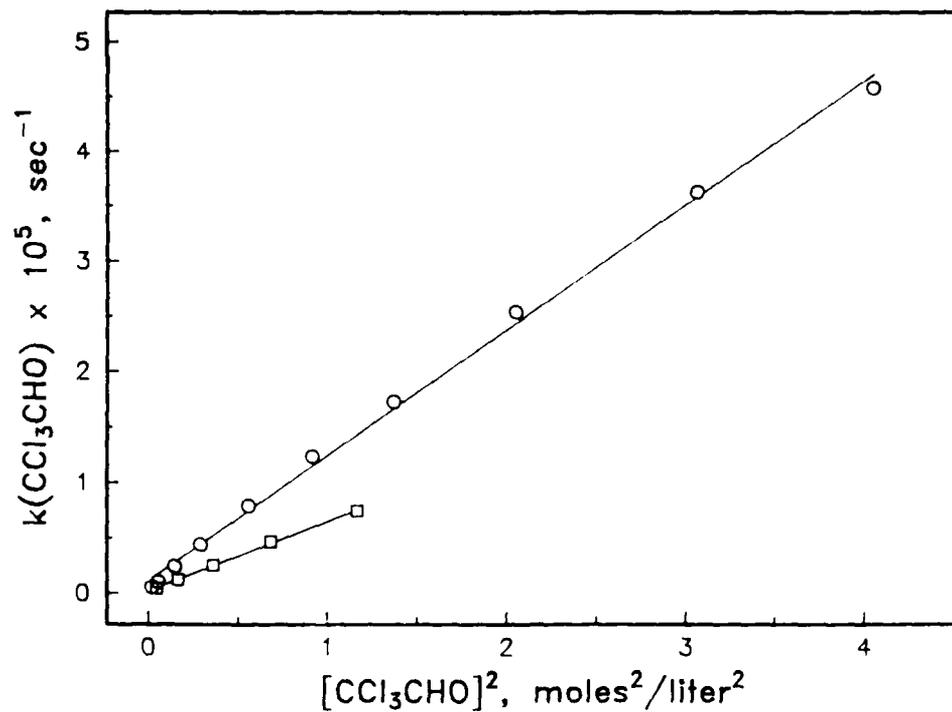
Figure 14. Correlation of the rate constant, k(CCl₃CHO), for peroxide decay with the square of the chloral concentration at 49.3° and 59.1°C
(○- 59.1°C; □- 49.3°C)

acetaldehyde, but for chloral, the titanous chloride appeared to react faster and the color developed much more rapidly. The rapid development of the color was found even when the highest concentrations of chloral were used. The observations suggested that the reaction intermediate formed from hydrogen peroxide and chloral was not as stable as those formed in solutions of formaldehyde and acetaldehyde. Assuming that the mechanism of the H_2O_2/CCl_3CHO reaction is basically the same as that for the $H_2O_2/HCHO$ reaction, i.e., Reaction 9, it would appear that the equilibrium constant, K_{eq}, for the H_2O_2/CCl_3CHO reaction is relatively small.

If the equilibrium constant, K_{eq}, in Equation 13 is very small, the $1/K_{eq}$ term in the denominator would be much greater than B^2 and the rate constant for peroxide decay could then be reduced to

$$k(CCl_3CHO) = k_{2c} K_{eq} (CCl_3CHO)^2 \qquad (22)$$

where k_{2c} is the rate constant for the unimolecular decomposition of the methylenehy-droxyperoxide derivative, $(CCl_3CHOH)_2O_2$. The results given in Figs. 13 and 14 are consistent with this rate expression. Fig. 15 shows the Arrhenius plot of the overall rate constant, $k_{2c}K_{eq}$, measured in the temperature range of 30° to $60^\circ C$.

The Arrhenius rate constant expression is

$$k_{2c}K_{eq} = 2.39 \times 10^5 \exp(-15,638/RT), \text{ liters}^2/\text{mole}^2\text{-sec} \qquad (23)$$

Writing the overall rate constant in the form of van't Hoff and Arrhenius expression gives

$$\text{Ln } k_{2c}K_{eq} = A + \Delta S/R - \frac{E + \Delta H}{RT} = 12.384 - \frac{15,638}{RT} \qquad (24)$$

where A is the Arrhenius preexponential, E is the activation energy, ΔH and ΔS are the enthapy and entropy of the reaction

$$H_2O_2 + 2 CCl_3CH(OH)_2 \rightleftharpoons (CCl_3CHOH)_2O_2 + 2H_2O \qquad (25)$$

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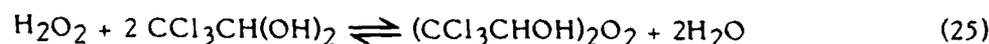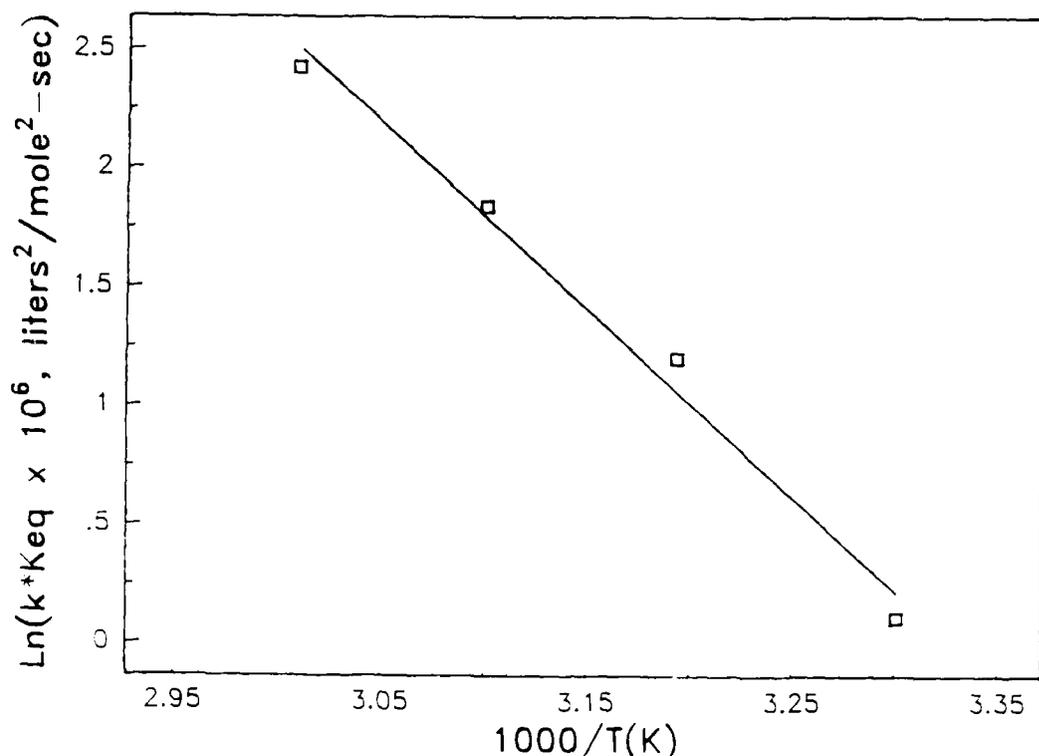
Figure 15. Arrhenius plot of the product, $k_c k_{eq}$, of the unimolecular rate constant and the equilibrium constant for the decomposition of the methylenehydroxyperoxide derivative formed in the reaction of hydrogen peroxide with chloral

and R is the ideal gas constant. Note that chloral is written in the hydrated form because the reaction is taking place in the aqueous phase. Equating the coefficients gives

$$A + \Delta S/R = 12.384$$

and

$$E + \Delta H = 15,638 \text{ cal/mole}$$

To determine unimolecular rate constant k_{2c}, it will be necessary to measure ΔS and ΔH of Reaction 25. ΔH could be determined calorimetrically; then ΔS could be calculated if the equilibrium constant was known at some defined temperature. It is conceivable that the equilibrium constant, K_{eq}, could be determined from a kinetic analysis similar to that used to calculate K_{eq} in the $H_2O_2/HCHO$ reaction. This may be accomplished by measuring the rate of disappearance of peroxide in solutions containing substantially higher concentrations of chloral than were used in the present work.

Thermochemistry

In view of the fact that substantial data with consistent quality are now available on the kinetics of the reaction of hydrogen peroxide with formaldehyde in aqueous solution, it is possible to calculate the thermochemical properties of methylenehydroxyperoxide. According to the results of this work, reaction between hydrogen peroxide and formaldehyde in aqueous solution is

$$H_2O_{2(l)} + 2H_2C(OH)_{2(l)} = (H_2COH)_2O_{2(l)} + 2H_2O_{(l)} \tag{26}$$
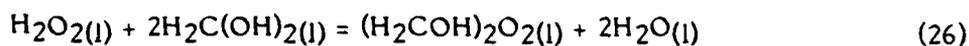
where l stands for the liquid phase.

It is important to note that formaldehyde is in the form of methylene glycol when it is dissolved in water. From the equilibrium constant determined for this reaction, the enthalpy and entropy are -8.43 kcal/mole and -19.2 cal/mole $^{\circ}K$, respectively. The pertinent thermochemical properties for hydrogen peroxide, methylene glycol, and water in their liquid states are given in TABLE 2.

TABLE 2. Thermochemical Data

Compound	H_{f300}	S_{f300}	Reference
$H_2O_{(l)}$	-68.32	16.75	(30)
$H_2O_{2(l)}$	-44.2	29.1	(30, 31)
$H_2C(OH)_{2(l)}$	-105.2	43.9	(30, 26)

The properties of methylene glycol in the liquid state were calculated from gaseous state data given by Benson (30) and data on the estimated heat of vaporization and boiling point reported by Walker.(26) Based on the results of the present study and known thermodynamic data, the enthapy and entropy of formation of methylenehyroxyperoxide were found to be $\Delta H_{f300} = -126.4$ kcal/mole and $\Delta S_{f300} = 64.2$ cal/mole $^{\circ}K$.

VI. CONCLUSIONS

The kinetics of the reactions of hydrogen peroxide with formaldehyde, deuterated formaldehyde, acetaldehyde, and chloral have been examined in aqueous phase in the temperature range of approximately 23° to $70^\circ C$.

The kinetics of these reactions were based, for the most part, on measurements of the rate of disappearance of peroxide. The kinetics were examined using low initial concentrations of hydrogen peroxide and relatively high concentrations of aldehyde, with the objective of measuring changes in the peroxide concentration while the aldehyde concentration remained essentially constant. Measurements of peroxide concentration versus time showed that the rate of peroxide disappearance was first order in the peroxide concentration for each of the aldehydes examined. These kinetic measurements were carried out at several aldehyde concentrations, and it was found that the rate constant for the disappearance of peroxide had a complex dependence on the concentration of aldehyde.

Measurements of amounts of carboxylic acid formed showed that each mole of hydrogen peroxide reacts with two moles of formaldehyde and/or deuterated formaldehyde. Similar measurements indicated that the number of moles of acetaldeyhe and chloral that react with each mole of hydrogen peroxide is equal to 2 in some cases, but in most of the experiments, it was found to be less than 2.

The principal gaseous products of the reactions with formaldehyde and deuterated formaldehyde are hydrogen and deuterium, respectively. Hydrogen and methane are formed in a two-to-one ratio in the reaction of hydrogen peroxide with acetaldehyde. Only hydrogen was detected in the reaction of hydrogen peroxide with chloral.

A kinetic model was developed to explain the first order rate of peroxide disappearance and the complex dependence of the rate constant for peroxide decay on the aldehyde concentration. The model was based on a two-step reaction; the first step being the formation of a methylenehydroxyperoxide-type intermediate from hydrogen peroxide and the aldehyde and the second being the decomposition of the intermediate into the carboxylic acid and gaseous products consisting mainly of hydrogen.

For the reaction of hydrogen peroxide with formaldehyde and deuterated formaldehyde, the equilibrium constants for the first step of the reactions and the unimolecular rate constants for the decomposition of methylenehydroxyperoxides were determined. The equilibrium constants were found to be $K_{eq} = 6.38 \times 10^{-5} \exp(8,425/RT)$, liters^2/mole^2 for formaldehyde and $K_{eq} = 0.153 \exp(3,894/RT)$, liters^2/mole^2 for deuterated formaldehyde. The unimolecular rate constants were $k_{2H} = 7.756 \times 12 \exp(-25,066/RT)$, sec^{-1} for formaldehyde and $k_{2D} = 1.408 \times 10^{12} \exp(-25,491/RT)$, sec^{-1} for deuterated formaldehyde.

The reaction of hydrogen peroxide with formaldehyde was found to be about 10 times faster than that with deuterated formaldehyde. A factor of 2 of this difference is attributed to the well known zero point energy effect used to explain isotope effects on rates of reactions. The remaining factor of 5 could be attributed to quantum tunneling. However, the data on the reaction of hydrogen peroxide with deuterated formaldehyde is limited and this conclusion is tenuous.

The thermodynamic properties of methylenehydroxyperoxide, calculated from its equilibrium constant, were found to be

$$\Delta H_{f300} = -126.4 \text{ kcal/mole, and } \Delta S_{f300} = 64.2 \text{ cal/mole } {}^{\circ}K$$

The rate controlling step in the reaction of hydrogen peroxide with acetaldehyde was also attributed to the decomposition of an intermediate similar to methylenehydroxyperoxide which was proposed in the formaldehyde reaction. A unimolecular rate constant for the decomposition of the intermediate was found to be

$$k_a = 2.25 \times 10^9 \exp(-22,095/RT), \text{ sec}^{-1}$$

The kinetics of the reaction of hydrogen peroxide with chloral was found to be second order in the chloral concentration. This result, which was in accordance with the model derived for the reaction of hydrogen peroxide with formaldehyde, showed that the equilibrium constant for the formation of the methylenehydroxyperoxide derivative, $(CCl_3CHOH)_2O_2$, was relatively small compared with that measured in the formaldehyde reaction. The rate constant for the reaction of hyrogen peroxide with chloral was found to be

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$$k_{2c}K_{eq} = 2.39 \times 10^5 \exp{(-15,638/RT)}, \text{ liters}^2/\text{mole}^2\text{-sec}$$

where the equilibrium constant, K_{eq}, is for the formation of the intermediate and the unimolecular rate constant, k_c, is for the decomposition of the intermediate.

VII. RECOMMENDATIONS

As a result of the work on this program, the following recommendations are made:

o   Further work is recommended on the reaction of hydrogen peroxide with deuterated formaldehyde. This reaction was found to be markedly slower than the analogous reaction of hydrogen peroxide with normal formaldehyde. The difference in the rates of the reactions of hydrogen peroxide with the deuterated and normal forms of formaldehyde was not reconciled with the accepted zero point energy theory. The tunnel effect has been offered as an explanation, but before definitive conclusions can be made, it is recommended that additional data should be obtained to increase the accuracy of the rate constant measurements. Those data are needed to improve the accuracy of the activation energy and the preexponential factor that indicate the relative importance of the respective zero point energy and tunnel effects.

o   It is recommended that additional work on the reaction of hydrogen peroxide with acetaldehyde and choral should be performed. Acetaldehyde is an important intermediate in the combustion of higher molecular weight alcohols such as ethanol, and it is possible that it might be the precursor to acetic acid in cool regions (cylinder walls, etc.) of an engine. The reaction of hydrogen peroxide with chloral is important to study in more detail because it will aid in understanding the mechanism of the acetaldehyde reaction. Only preliminary measurements were made in the present study on the rate of the hydrogen peroxide/acetaldehyde reaction. A more thorough experimental investigation of the reactions of hydrogen peroxide with acetaldehyde and chloral is needed before a more generalized mechanism can be proposed for the reactions of hydrogen peroxide with aldehydes.

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Several studies have shown that low-temperature operation of spark ignition engines on methanol fuel results in unusually high ring and cylinder bore wear. It has been found that the wear is caused by formic acid and peroxide formed in the low-temperature combustion of methanol. Bench studies have shown that combustion residues are formed when shallow pools of alcohols are burned. The residues were found to contain substantial concentrations of aldehydes, carboxylic acids, and peroxides. The objective of the present study was to measure rates and to determine the kinetics of formation of carboxylic acids and peroxides observed in residues formed by burning shallow pools of liquid alcohols.

An examination of the literature suggested strongly that carboxylic acid formation in alcohol combustion was probably caused by the reaction of hydrogen peroxide with aldehydes, Since it was

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not clear whether carboxylic acids are formed in the gas phase or the liquid phase (in the combustion residue), the reaction of hydrogen peroxide with aldehydes was first studied in aqueous solution. The rate of reaction was followed by measuring the rate of decay of the total peroxide concentration. Note the term total peroxide includes all peroxides, i.e., hydrogen peroxide, methylenehydroxyperoxides, and peracids such as performic acid. Carboxylic acid concentrations were measured at the end of the reaction after most of the peroxide was consumed. Reactions were carried out using low concentrations of hydrogen peroxide and relatively high concentrations of aldehyde. In this way, changes in the concentrations of peroxide could be measured while the concentration of aldehyde could be assumed to be essentially constant.

The kinetics of the reactions of hydrogen peroxide with formaldehyde, deuterated formaldehyde, acetaldehyde, and chloral were examined in aqueous solution. The rate of disappearance of peroxide was found to be first order in the total peroxide concentration in all of the above-mentioned reactions. For formaldehyde and deuterated formaldehyde, the rate constant for peroxide decay was of complex function of the aldehyde concentration. A kinetic model was derived that explained the complex dependence of the reaction rate on aldehyde concentration. The model was based on the formation of a methylenehydroxyperoxide-type intermediate that rapidly built up to its equilibrium concentration and then decomposed at a relatively slow rate. It was assumed in the model that the only route for peroxide decomposition was through the methylenehydroxyperoxide intermediate. Other routes such as the decomposition of hydrogen peroxide were about two orders of magnitude slower than the peroxide decay rates measured when formaldehyde was present in solution. In the reaction of hydrogen peroxide with chloral, the disappearance of peroxide was dependent on the square of the aldehyde concentration. This second order dependence of the rate constant or peroxide decay on the chloral concentration was explained with the kinetic model by assuming that the equilibrium constant for the formation of the intermediate methylenehydroxyperoxide derivative was very small compared to that in solutions containing hydrogen peroxide and formaldehyde. The reaction of hydrogen peroxide with acetaldehyde was also a complex function of the acetaldehyde concentration. The results on the acetaldehyde reaction seem to be elucidatable by the kinetic model, but there are some unanswered questions that must be addressed before definite conclusions can be made.

Rate constants and equilibrium constants are given in the report for the respective decompositions and formations of the methylenehydroxyperoxide-type intermediates proposed to exist in the reactions of hydrogen peroxide with aldehydes.