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Prepared for the
Office of Naval Research
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Kinetics of the Initial Reaction Between an Aldehyde and Hydrogen Peroxide in Aqueous Solution

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Abstract:

Hydrogen peroxide, water, and low molecular weight aldehydes are commonly-encountered species in the products of the homogeneous partial oxidation of gaseous hydrocarbons. A knowledge of the kinetics of their mutual reactions can increase our understanding of the separation and manipulation of such products. The present study was focused on the reaction of hydrogen peroxide with acetaldehyde, but some studies were also made of its reaction with formaldehyde and propionaldehyde.

The reaction with acetaldehyde is homogeneous, acid catalyzed, and does not appear to involve free radicals under the conditions studied. The reaction rates of all three aldehydes were found to be proportional to the hydrogen peroxide concentration and to the two-thirds power of the aldehyde concentration. The reaction rate increased in the order: formaldehyde, acetaldehyde, propionaldehyde, and this is interpreted in terms of the degree of hydration of the three aldehydes.

Certain observations on separation of partial oxidation products are interpreted in terms of the reactions studied.

An increasing industrial interest is being directed to partial oxidation of gaseous hydrocarbons as the basis for methods of manufacture of various chemicals. Aldehydes are almost always present in the products of such reactions, particularly formaldehyde and acetaldehyde, and hydrogen peroxide is also formed in most cases of homogeneous reaction, although whether or not it is isolated depends upon the experimental conditions. Cooling the oxidation products thus may yield a condensate containing primarily aldehydes, water, and hydrogen peroxide, plus perhaps other oxygenated products.

The problem of separation of this mixture is greatly complicated by the fact that the aldehydes and hydrogen peroxide react in the liquid phase to form hydroxy alkyl peroxides as shown in equations 1 and 2

$$RCHO + H_2O_2 \rightleftharpoons RCH(OH)OOH \qquad (1)$$

$$RCH(OH)OOH + RCHO \rightleftharpoons RCH(OH)OOCH(OH)R \qquad (2)$$

The dialkyl peroxide may also take part slowly in further reactions leading to organic acids and other products. The equilibria of reactions (1) and (2) have been reported (7) for both formaldehyde and acetaldehyde. For acetaldehyde the equilibrium constants are:

$$K_1 = 0.0208 \text{ mole/liter} = \frac{(H_2O_2)(CH_3CHO)}{(CH_3CH(OH)\,OOH)}$$

$$K_2 = 0.00204 \text{ (mole)}^2/\text{(liter)}^2 = \frac{(H_2O_2)(CH_3CHO)^2}{(CH_3CH(OH)OOCH(OH)CH_3)}$$

The kinetics of the reactions between formaldehyde and aqueous hydrogen peroxide have been studied (6) but relatively little information has been published on the equivalent reactions with acetaldehyde. The kinetics of such reactions are of interest in conjunction with the separation and other problems associated with many hydrocarbon partial oxidation studies; for example to help determine the feasibility of removing hydrogen peroxide from the system before appreciable quantities become bound up with aldehydes. The present investigation was therefore undertaken with primary attention being given to the reaction with acetaldehyde. A few studies were also made on formaldehyde and propionaldehyde.

EXPERIMENTAL

At least five methods might be used to analyze the system under study. They are (1) determination of free acetaldehyde by titration using the hydroxylamine hydrochloride-sodium hydroxide method, (2) spectrophotometric determination, (3) determination of free hydrogen peroxide by the perborate method (7), (4) polarographic determination, (5) calorimetric determination. There is some doubt as to the accuracy of the perborate method, since a substantial length of time is required for the analysis during which the concentrations in the solution under study might change appreciably. Both the polarographic and calorimetric

determinations require special apparatus which was not readily available.

The hydroxylamine hydrochloride-sodium hydroxide method and the spectrophotometric method were chosen for use in this investigation. Both are relatively rapid, and the equipment for use in each was relatively readily available.

A. Hydroxylamine Hydrochloride-Sodium Hydroxide Procedure

A dilute aqueous solution of hydrogen peroxide was mixed with a dilute aqueous solution of acetaldehyde. The solutions had previously been analyzed for their respective constituents, the hydrogen peroxide by a $KI-H_2SO_4-Na_2S_2O_3$ titration, the acetaldehyde by adding it to an aqueous solution containing excess hydroxylamine hydrochloride and titrating the freed acid with sodium hydroxide. The concentration of acetaldehyde was determined at definite time intervals in aliquots taken from the main solution, using the hydroxylamine hydrochloride-sodium hydroxide titration, and bromphenol blue as the indicator. This technique was used for runs made at room temperature, and also on runs made with solutions cooled with ice-water mixture, and kept at ice temperature. The temperatures of the reacting solutions were not measured, either before or after the run. In the case of the runs made at room temperature, the room temperature during the run was recorded.

It was found that peroxides in the analysis sample slowly reacted with the hydroxylamine hydrochloride, liberating acid. Consequently, after reaching the end point, the solution which

had been titrated was allowed to stand for a time interval equal to that required for reaching the first end point, and then a second end point was determined. This provided a slight correction for the side reaction.

This chemical method was used for the studies with acetaldehyde, the results of which are given in Figures1 and 2, and for studies to determine the effect of glass wool and ferric ion on the reaction rate. It was also used for the propionaldehyde reaction studies reported in Figure 3.

B. Spectrophotometric Procedure

The use of this technique rests on the fact that in the spectral range of 2900-3200°A the absorptivity in this system is principally that of the carbonyl group, and therefore the degree of absorptivity decreases as reaction proceeds. From the equilibrium data available it is apparent that, besides water, the only species which will be present in significant amounts are hydrogen peroxide, acetaldehyde, and the mono-alkyl addition product, $CH_3CH(OH)OOH$. The spectrophotometer was calibrated by measuring the optical densities for pure aqueous solutions of hydrogen peroxide and of acetaldehyde, each of various concentrations. The absorptivity of the mono addition product was determined by mixing equi-molal quantities of concentrated hydrogen peroxide and acetaldehyde, allowing reaction to proceed, diluting with water, and determining the absorption spectrum

of the solution between 2500 and 3500°A. The absorptivity was found to equal 80% of that of hydrogen peroxide over the spectral range. The assumption that the solution contains essentially the mono addition product is justified by the equilibrium data and by the fact that no hump was shown in the curve at about 2850-2900°A where acetaldehyde has a strong absorption band. Moreover, the calculated rate constants are not very sensitive to the percent absorptivity taken for the mono addition product, because of the strong absorptivity of the carbonyl group in the free acetaldehyde. For example, if the mono-addition product absorptivity were 70% rather than 80% of that of hydrogen peroxide, it would change the rate constant by only 3-5%.

In making the runs, dilute solutions of the reactants were mixed, then an aliquot was pipetted into a quartz cell which was placed immediately in the spectrophotometer. (A Cary Double-Beam Recording Spectrophotometer was used throughout the investigation). A continuous record of the ultra violet light absorption by the solution was taken, starting as soon as the cell was placed in the instrument, and lasting, in most cases, until the reaction had gone essentially to completion.

For each run, a particular wave length in the range of 2900-3200°A was picked, so chosen as to give maximum accuracy for the concentrations studied in that particular run. Hydrochloric

acid was added to catalyze the reaction in certain runs, as noted below. The spectrophotometer method was used for the studies reported in Table 1 and also for the studies with formaldehyde, reported in Table 2.

Temperatures could not be measured in the cell itself, so the values reported are those of the thermostatted bath.

RESULTS

As discussed below, it was found that with all three aldehydes the kinetic data were best fitted by assuming that the forward reaction is first order with respect to hydrogen peroxide and two-thirds order with respect to the aldehyde. If subsecuent reaction of the mono-addition product and back reactions are neglected, the resulting rate expression: $dc/d\theta = k(b)(a)^{2/3}$ can be integrated, giving:

$$\theta k = -\frac{1}{2(b_o-a_o)^{2/3}}\left\{3\ln\left[(b_o-a_o)^{1/3}+(a_o-c)^{1/3}\right]-\ln(b_o-c)\right.$$

$$\left.-\frac{3}{(b_o-a_o)^{2/3}}\tan^{-1}\left[\frac{2(a_o-c)^{1/3}-(b_o-a_o)^{1/3}}{\sqrt{3}\,(b_o-a_o)^{1/3}}\right]\right\}+\text{constant}$$

where:
- k is the rate constant
- θ is the time in minutes
- a is concentration of acetaldehyde
- a_o is concentration of acetaldehyde, initially
- b is concentration of hydrogen peroxide
- b_o is concentration of hydrogen peroxide, initially
- c is concentration of mono-addition product

and concentrations are given in gm. mole/l.

The values of $k\theta$ were plotted against time, θ for that

part of the reactio corre onding to up to 30-50% of equilibrium. The rate constant wa n as the slope of the best curve through the points for the first few minutes, neglecting initial transient conditions. The constant k is given in the units $(\text{g. moles/liter})^{2/3}(\text{min})^{-1}$.

Figure 1 shows the results of studies with acetaldehyde at about 28°C. using the chemical method of analysis. Initial concentrations of hydrogen peroxide and acetaldehyde of from 0.04 to 0.10 molar were used here. Figure 2 shows the results of similar studies at 0°C; here the initial concentrations of the reactants varied from 0.06 to 0.20 molar. The spectrophotometric runs with acetaldehyde are given in Table 1. (Note that hydrochloric acid was added in four of these runs). Two runs made with formaldehyde are given in Table 2. The results of the studies with propionaldehyde, in which chemical analysis was used, are given in Fig. 3.

From the chemical-analysis studies the value of k for acetaldehyde, as calculated above, is about 0.67 at 28°C. From the spectrophotometric studies on acetaldehyde, the best value of k is 0.61 at 25°C. At 0°C, the value of k is about 0.066. For formaldehyde, k is about 0.11 at 25°C., and for propionaldehyde k is about 0.75 at 20°C. The data on acetaldehyde at the two temperatures indicate an activation energy of 14 kcal/mole.

TABLE I

SPECTROPHOTOMETRIC RUNS: ACETALDEHYDE

Run	Temp. (°C.) *	Initial Conc. CH_3CHO (M./l.)	Initial Conc. H_2O_2 (M./l.)	Reaction Rate Constant k	HCl Added (M./l.)
1	25	0.264	0.293	0.61	---
2	25	0.154	0.342	0.62	---
3	25	0.289	0.128	0.60	---
4	25	0.172	0.152	0.60	---
5	25	0.62	0.68	0.76	---
6	25.1	0.0786	0.0392	0.61	---
7	25.1	0.0393	0.0785	0.61	---
8	25.9	0.189	0.121	4.10	0.015
9	26.2	0.0137	0.00795	0.57	---
10	26.2	0.0137	0.00795	8.7	0.097
11	26.2	0.0137	0.00795	1.3	0.015
12	26.2	0.0137	0.00795	5.1	0.040
13	25	1.79	0.90	1.05	---
14	25	0.89	1.80	0.94	---

* Note: Runs 8-12 not thermostated.

TABLE II

SPECTROPHOTOMETRIC RUNS: FORMALDEHYDE

Run	Temperature (°C)	Initial Concentration H_2O_2 (mol/l.)	Initial Concentration CH_2C (mol/l.)	Reaction Rate Constant
1	25.0	1.27	8.6	0.116
2	25.0	1.18	0.86	0.111

To determine the possible contribution of heterogeneous processes, a run was made at 22°C. in which a quantity of glass wool of 10 micron diameter was added to the flask. Initial concentrations were 0.0241 molar hydrogen peroxide, 0.0474 molar acetaldehyde and the area of the glass wool was estimated at 4000 sq. cm. as compart to about 160 sq. cm. for the reaction flask alone. The results gave a rate constant of 0.66, from which it may be concluded that the glass surface makes no contribution to the reaction.

To investigate the possibility that the reaction is free radical in nature, two different tests were made at 22°C on the system water-acetaldehyde-hydrogen peroxide. The first procedure used was to add 10 parts per million of ferric ion to the reacting solution. Since it is generally believed that ferric ions catalyze the formation of OH radicals from hydrogen peroxide, it was thought that perhaps this addition would have an effect on the reaction rate. (This concentration of ferric ion was found to decompose about 5% of a 0.3M solution of hydrogen peroxide in one hour.) The analyses in these tests were by the chemical method. Secondly, a strong mercury-vapor lamp was placed above a beaker containing the reacting solution, and the rate determined by chemical analysis. Reactant concentrations were approximately as above. In the ferric ion run, k was found to be 0.67; in the run with ultraviolet radiation, k was 0.41.

In another study a run was made using the spectrophotometer equipment in the usual fashion except that the ultra-violet source was directed through the reacting solution only during a few brief intervals in which measurements were taken, rather than continuously. No significant difference in the results was noted. It therefore is highly probable that under the conditions studied the reaction is not free-radical in character, and that the ultra-violet radiation of the spectrophotometer had no significant effect on the results.

The runs using added hydrochloric acid establish that the reaction is acid-catalyzed, but insufficient data were obtained to formulate a rate equation to include this effect.

Reagent grade chemicals were used for all studies. The acetaldehyde was found to have a small acid content, amounting to an average of 1.3% of the acetaldehyde present. The effect of this acid content on the rate constants reported is probably small. If it is assumed to be acetic acid and the reaction rate is assumed, as an approximation, to have the same dependency on the hydrogen ion concentration as that exhibited with hydrochloric acid, this would amount to a correction of 10-20% of the value of k reported. The propionic acid present in the propionaldehyde used was less than 0.6%. The acid content of the formaldehyde used was not determined but since aqueous solutions of formaldehyde are fairly stable, the acid concentration was probably very low.

No corrections for acid catalysis were made to any of the data reported.

DISCUSSION

Figures 1 and 2 show the reproducibility of the chemical analysis method. The change in slope of the curve of Figure 1 after about 5 minutes time can be attributed to the reverse reaction. In Figure 2 the runs seem to start at a time of -3 minutes. The cause was a temperature rise of the reactants above 0°C during the pipetting and other manipulative procedures at the beginning of a run which produced a more rapid reaction before the solution was cooled back down to 0°C. Likewise in Table 1, a few runs using high concentrations gave somewhat higher values of k, presumably due to the rapid rate of the initial reaction which would elevate the temperature of the mixture slightly above that of the bath. The close correspondence between the results obtained with the two methods of following the reaction gives confidence as to the reliability of the rate constants obtained.

It might have been expected that the reaction would be first order with respect to both hydrogen peroxide and acetaldehyde. However, the data obtained with all three aldehydes instead closely fit a two-thirds order expression for the aldehyde. The evidence for this conclusion is best seen in the results of Table 1, in which the various runs cover initial hydrogen peroxide

and acetaldehyde concentrations each varying by a factor of over 100.

An assumption that the acetaldehyde concentration should enter the rate expression as either the one-half or first power leads to a very considerable scatter of the values of k thus calculated. In this connection it is interesting to examine the results of Duniez, Perrin, and Style on the rate of reaction of formaldehyde and hydrogen peroxide (6). They reported their kinetic data fitted to a second order equation, but a recalculation assuming a two-thirds order for the formaldehyde brings their results much closer together. This has been done in Figure 4. The values of kθ as they calculated them are shown for the two runs they reported, (which were made in the presence of 0.0025M sulfuric acid). The reaction rate constants are seen to be significantly different for the formaldehyde concentrations which varied by a factor of two. Also shown are their original data multiplied by the original formaldehyde concentration to the one-third power, to obtain a k conformable to a two-thirds order rate expression. It is seen that this brings their calculated results quite close together. The new value of k thus calculated is about 0.05, which is one-half of the value found in the present work.

Most of the difference between these two values is caused by the difference between the absorptivity ascribed to the

mono-addition product of hydrogen peroxide and formaldehyde. Dunicz, Perrin, and Style took it to be 50% of that of hydrogen peroxide, while in the present work it was assumed to be 80%, based on the studies with acetaldehyde. The calculated value of the rate constant is much more sensitive to the absorptivity assumed for the addition product in the case of the formaldehyde reaction than of the acetaldehyde reaction, since formaldehyde is almost 100% hydrated in aqueous solution. The absence of the carbonyl group causes the hydrated formaldehyde to have relatively little absorptivity. The rate constant of Dunicz, Perrin, and Style as recalculated above may be compared with that obtained here by (1) allowing for the difference in assumed absorptivity of the mono-addition product, and (2) adjusting their rate constant for the 0.0025M sulfuric acid concentration present in their runs, using their rate expression for the effect of the acid. If this is done, their rate constant and the one obtained here become identical.

The two-thirds order with respect to the aldehyde indicates that the reaction is probably fairly complex, rather than the simple one which has been accepted (6). Such a rate expression is awkward to interpret kinetically, and may be associated in some way with polymer formation in solution. The fact that the reaction follows the two-thirds order expression for the aldehyde over the wide concentration range studied, and

for all three aldehydes makes it highly unlikely that simultaneously-occurring reactions were being observed.

The rate constants obtained show that the rate of reaction of an aldehyde with hydrogen peroxide increases in the order: formaldehyde, acetaldehyde, propionaldehyde. It might have been expected that the reverse would be true, if the species were each present in solution in the monomeric form, since presumably the steric factor would become smaller with increasing molecular complexity. However, it is known that formaldehyde is almost 100% hydrated in aqueous solution (4) and that acetaldehyde is about 55% hydrated at 25°C (1). Presumably propionaldehyde is less hydrated than acetaldehyde. It would be expected that the reaction of the carbonyl group with hydrogen peroxide might be similar to that with water. In the studies here the aldehyde has previously reached an equilibrium degree of hydration, and it seems reasonable to postulate that the hydrogen peroxide reacts only with the unhydrated form of the aldehyde. The differences in the relative reaction rates of the three aldehydes can then be attributed mainly to the fraction of the specie in each case which is present in the unhydrated form capable of reaction.

On cooling and condensing the products from the partial oxidation of a hydrocarbon, the aldehydes will presumably exist

initially in the unhydrated form. If hydrogen peroxide is also present, the hydration and peroxide-addition reactions will then presumably compete for the free aldehyde. Apparently no studies have been published on the rate of hydration of formaldehyde, but some information is available on that of acetaldehyde (2,3). For example, at 0°C the half-time for the hydration of a 0.4M concentration of acetaldehyde in neutral water solution is about 8 minutes (2). This is roughly four times as rapid as the hydrogen peroxide addition reaction at this concentration and temperature.

The rates of these various reactions greatly affect the results obtained when it is attempted to separate the products of a hydrocarbon partial oxidation reaction by fractional condensation. For example, in a previous study (8) it was found that the partial pressure of formaldehyde in the product gas leaving the condenser at various condenser temperatures was substantially less than the equilibrium partial pressure of formaldehyde above the aqueous solution formed, although the acetaldehyde partial pressure closely followed the theoretical values at all condenser temperatures studied. A reasonable explanation of these results is the postulation that during the residence time in the condenser a substantial amount of formaldehyde addition product with hydrogen peroxide was formed but not that of acetaldehyde. This addition product would

presumably have a lower volatility than formaldehyde hydrate. In the studies reported here, the peroxide addition reaction to hydrated aldehydes was less rapid for formaldehyde than acetaldehyde, but the reverse could readily be true when the aldehydes are initially in the unhydrated form. It is also possible that gas or liquid-phase polymerization of formaldehyde can account for some of these observations, although the polymerization rates appear to be much slower than the addition reactions.(5) It would be interesting to test some of these hypotheses by determining the hydration rates of formaldehyde, and the reaction rates of hydrogen peroxide with unhydrated formaldehyde and acetaldehyde in a medium which is non-solvating and non-polar.

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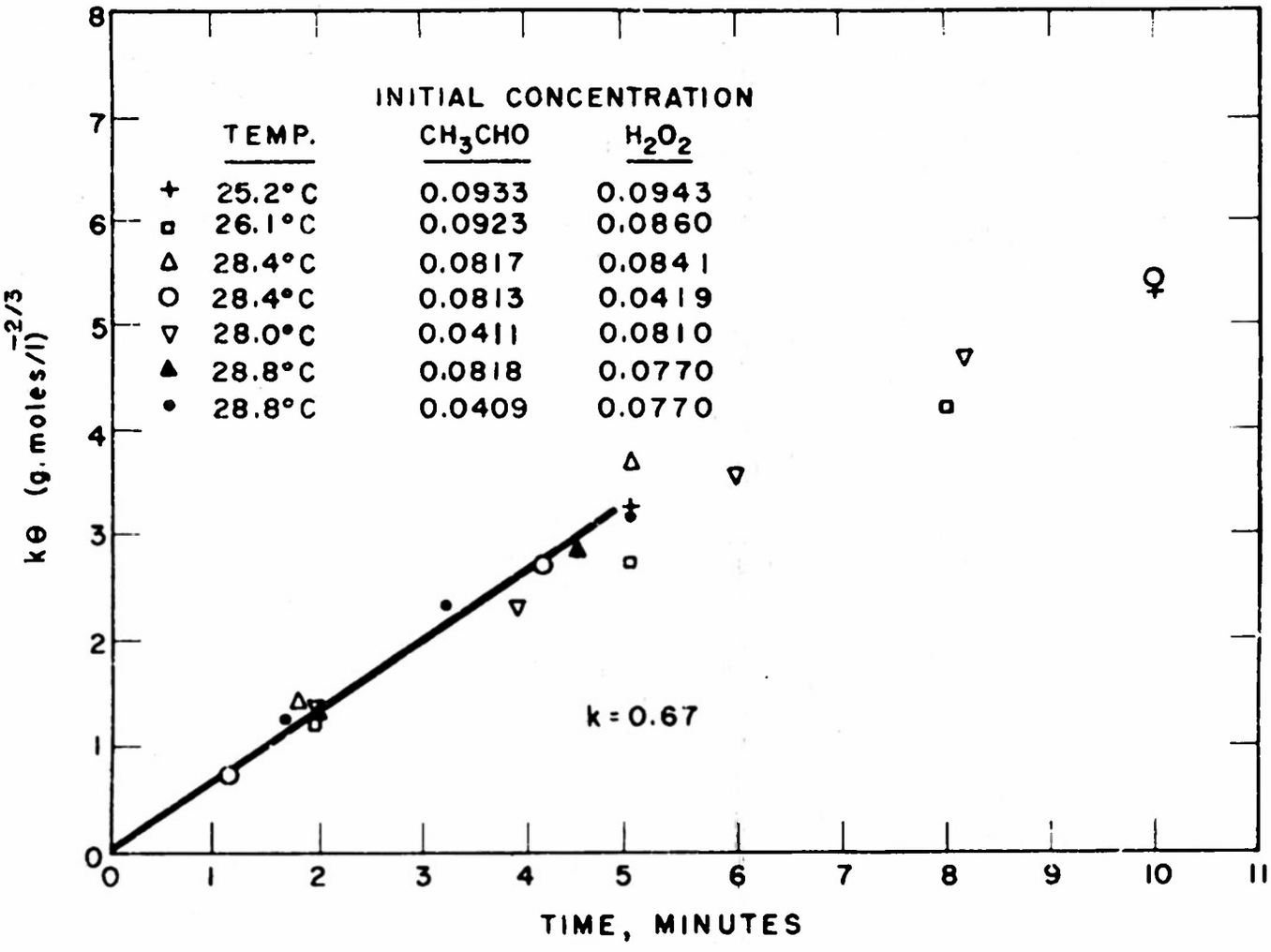

FIGURE 1 ACETALDEHYDE RUNS

(CHEMICAL ANALYSIS METHOD, ROOM TEMP.)

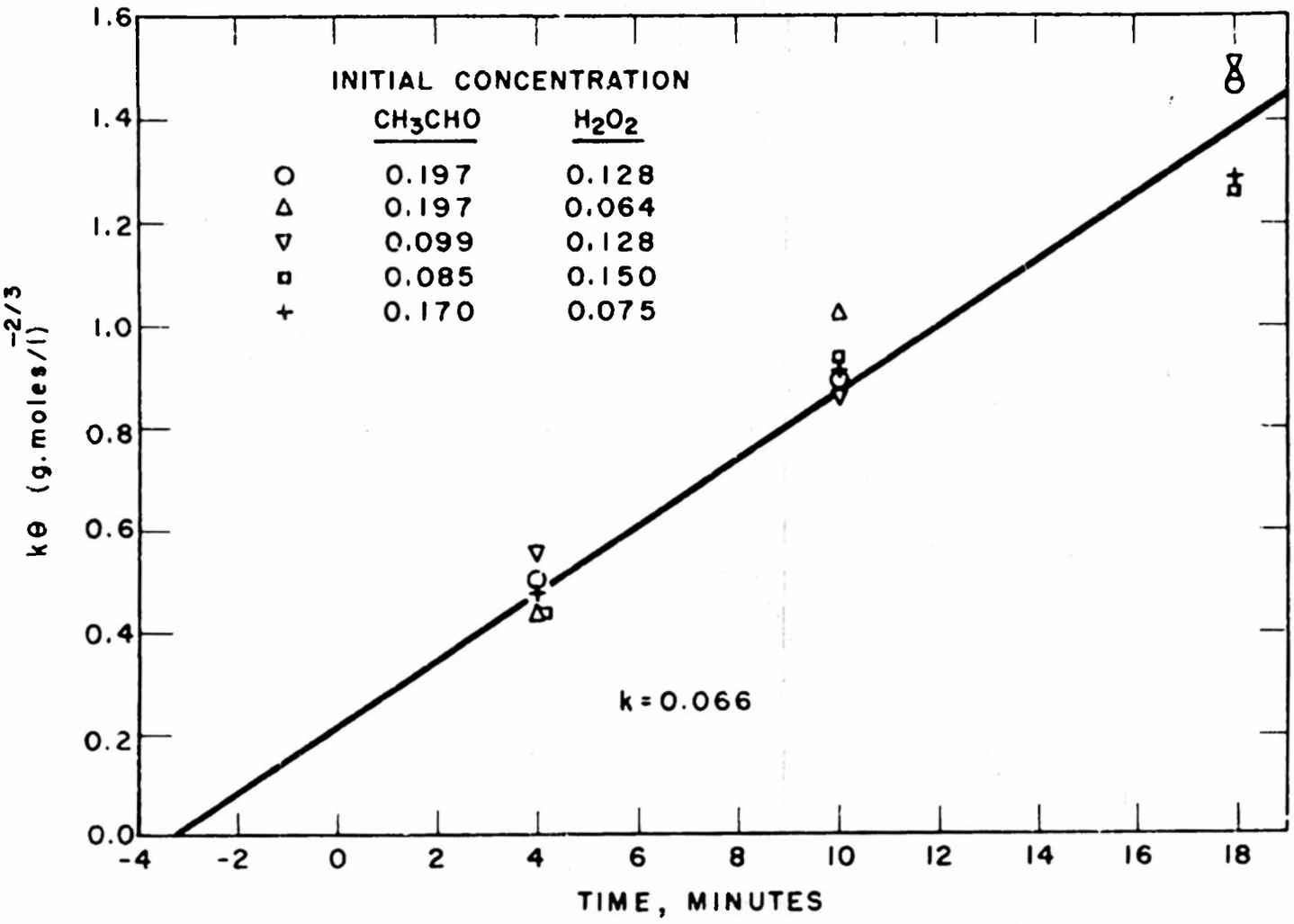

FIGURE 2 ACETALDEHYDE RUNS

(CHEMICAL ANALYSIS METHOD, ICE-BATH TEMP.)

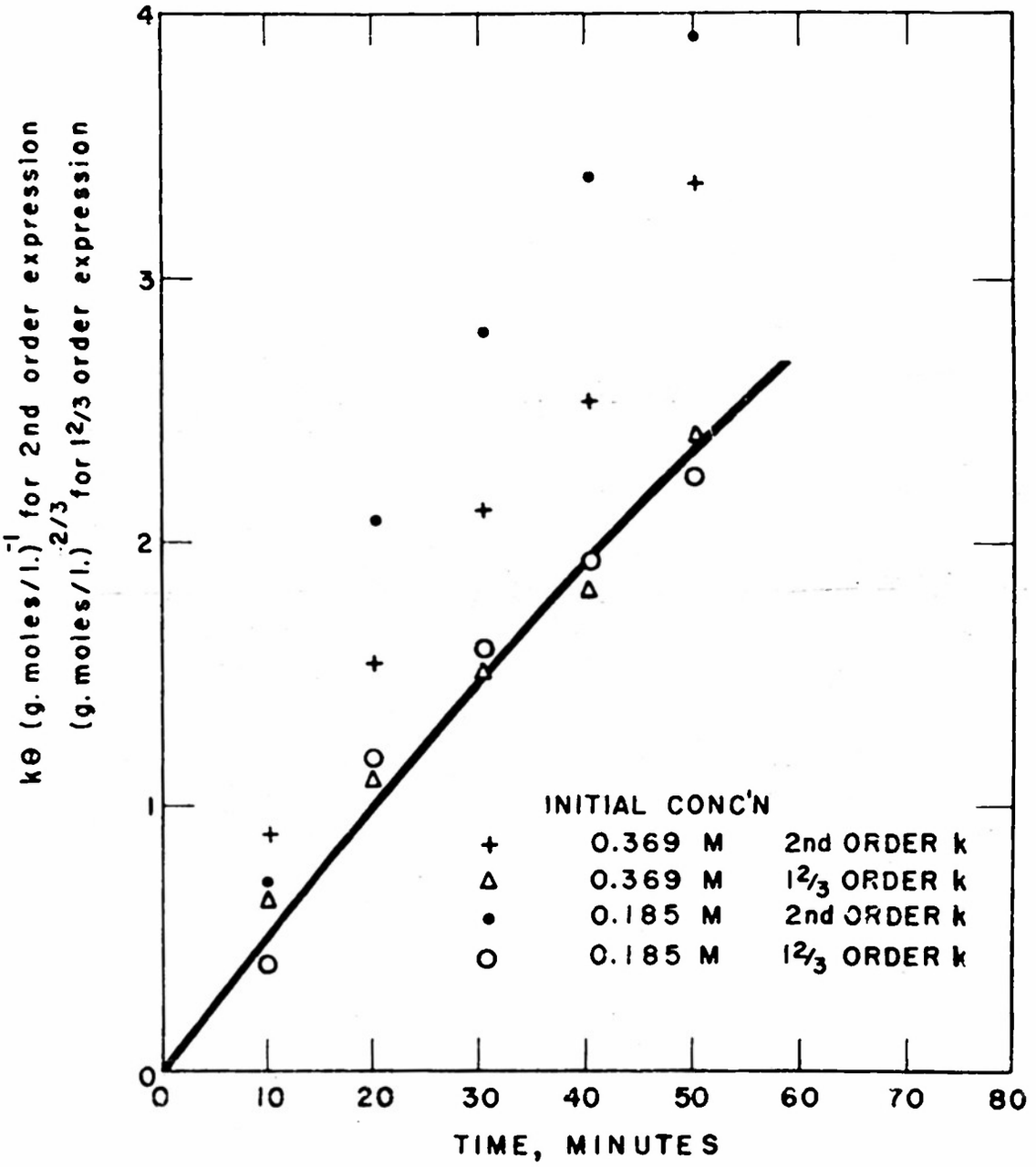

FIGURE 4 FORMALDEHYDE RUNS
(DATA OF DUNICZ, PERRIN, AND STYLE, REF. 6)

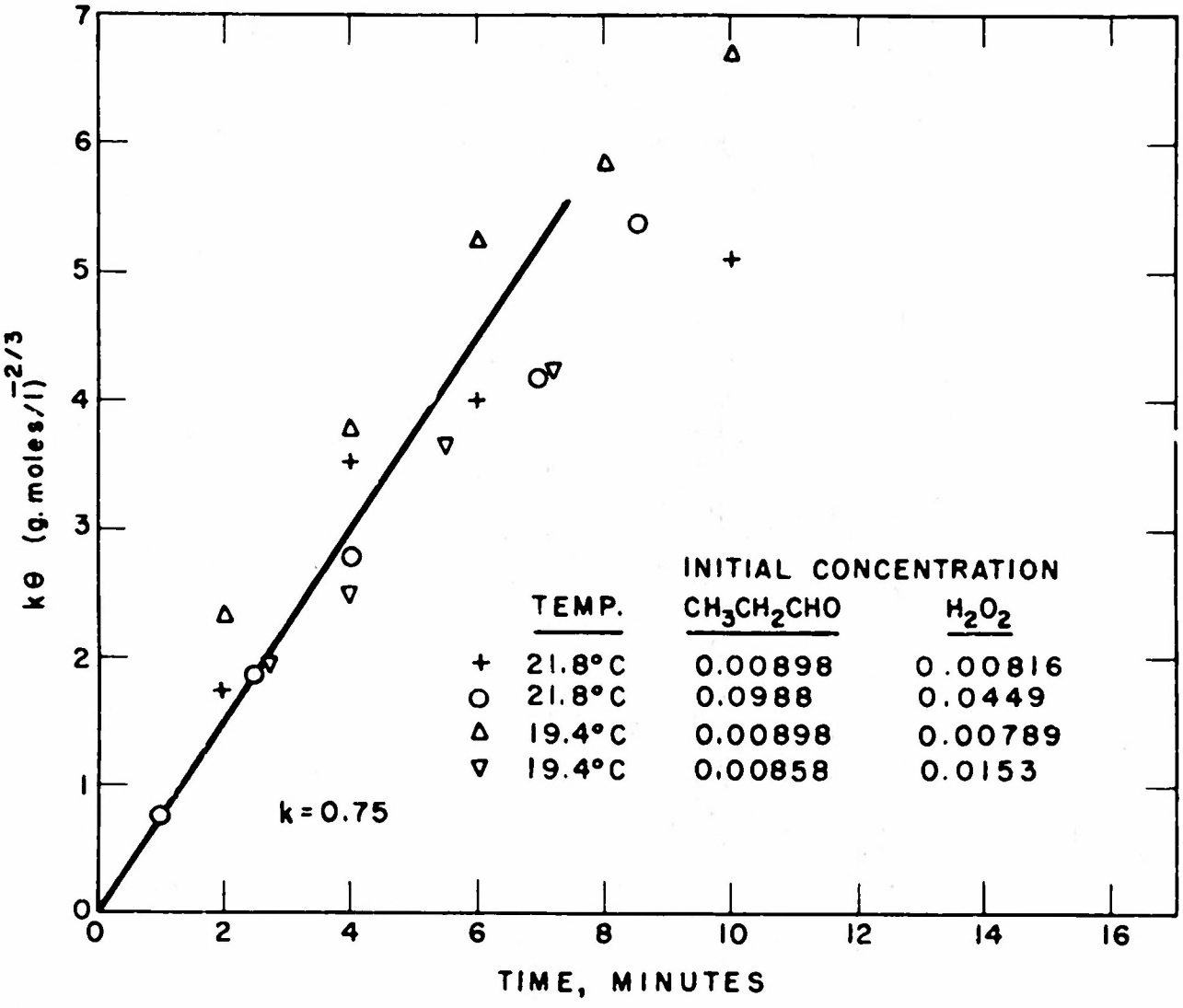

FIGURE 3 PROPIONALDEHYDE RUNS