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Destruction of Oxalate by Reaction with Hydrogen Peroxide

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Chemical Technology Division

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ABSTRACT

The destruction of oxalate by oxidation to carbon dioxide using hydrogen peroxide was studied as an alternative method for the disposal of oxalate in connection with the possible use of an aqueous hydrazine oxalate solution as a scrubbing agent for solvent cleanup in processes for the recovery of uranium, plutonium, and thorium by solvent extraction. The rate of oxidation of oxalate by hydrogen peroxide in acid solution at the reflux temperature was adequate for process application; reaction half-times at 100°C were less than one hour when the hydrogen peroxide concentration was greater than 0.5 M. The reaction was first order with respect to both the oxalate and hydrogen peroxide concentrations and had an activation energy of 58.7 kJ/g-mol. The rate increased with the hydrogen ion concentration as $[H^+]^{0.3}$ but was not significantly affected by the presence of 100 ppm of uranium or copper in solution. In the near-neutral hydrazine oxalate solutions, the reaction of either component with hydrogen peroxide was too slow for process application.

1. INTRODUCTION

The solvent extraction system in a fuel reprocessing facility uses tri-n-butyl phosphate (TBP) dissolved in a normal paraffin hydrocarbon diluent to recover uranium, plutonium, and thorium from a nitric acid solution. Radiolysis and hydrolytic reactions with nitric acid form acidic degradation products: principally dibutyl and monobutyl phosphoric acids. These degradation products and the metal-ion complexes between the degradation products and actinides or fission products must be removed from the organic phase to maintain the solvent quality. The standard cleanup method is to scrub the solvent with a sodium carbonate solution; however, this generates large quantities of sodium nitrate as a solid waste. An alternative scrubbing system using hydrazine carbonate has been developed,[1] but this solution presents some complications in the preparation technique and in decomposition since it evolves CO_2 spontaneously. Another promising scrubbing system uses hydrazine oxalate solutions.[2] This solution is readily prepared from hydrazine hydrate and oxalic acid and is quite stable. A possible difficulty is disposal of the reasonably stable oxalate component if it cannot be accommodated in normal handling of the aqueous waste stream. Oxalate can be oxidized by boiling, concentrated nitric acid,[3-4] but the reaction is slow and would require the addition of large quantities of acid to the spent scrub solution. An attractive alternative is to react the oxalate with hydrogen peroxide in a slightly acidic solution.[5-7]

The primary goal of the current studies was to determine the reaction kinetics of oxalic acid with hydrogen peroxide over the range of possible process conditions. The reaction between near neutral hydrazine oxalate solutions and hydrogen peroxide was also examined in a few tests.

In this work, the term oxalate (Ox) denotes the sum of the oxalic acid (H_2Ox), hydrogen oxalate ion (HOx^-), and the oxalate ion (Ox^{2-}) species.

2. EXPERIMENTAL

2.1 Materials

Reagent grade chemicals, oxalic acid, aqueous 85% hydrazine hydrate solution, 30 vol % hydrogen peroxide, azeotropic nitric acid (15.8 $\underline{M}$), and distilled water were used to prepare the solutions for this study. The oxalic acid was first dissolved in water to give a 0.825 $\underline{M}$ stock solution. The hydrazine oxalate solutions were prepared by adding the oxalic acid stock solution to 3.3 $\underline{M}$ hydrazine hydrate solution and diluting to obtain an approximately 0.5 $\underline{M}$ hydrazine oxalate stock solution.

2.2 Procedure

The kinetics of the reaction were investigated at 25, 60, and 90°C. In the experiments at 25°C, the total aqueous volume was 50 mL; in making up the solution, the order of addition was nitric acid, hydrogen peroxide, the oxalic acid stock solution, and water to make 50 mL of solution. The solution was stirred by a magnetic stirrer, and 2-mL samples were taken for analysis at timed intervals. The concentrations of nitric and oxalic acids were determined by titration immediately after sampling using a Brinkmann model E536 automatic titrator (Metrohm AG, Herisau, Switzerland). Samples to be analyzed for hydrogen peroxide content were cooled in an ice bath and delivered to the Analytical Chemistry Division laboratories where the peroxide concentration was determined by permanganate titration. Hydrogen peroxide was not determined in the tests at 25°C. In the tests at 60 and 90°C, 200-mL aqueous volumes were contained in boiling flasks which were equipped with reflux condensers and submerged in a controlled-temperature bath. The test solutions were prepared by adding the nitric acid to the water contained in the flask and then the hydrogen peroxide when the temperature reached 60°C; the oxalic acid or hydrazine oxalate solutions were added at the operating temperature, either 60 or 90°C. A few test solutions contained small quantities of dissolved copper or uranium; these were added at the same time as the oxalic acid. From start-up time to oxalic acid or hydrazine oxalate addition usually took 1 to 1.5 h; the time between the hydrogen peroxide addition and the oxalic acid or hydrazine oxalate addition was 20 to 40 min. The experiments were timed starting with the introduction of the oxalic acid or hydrazine oxalate (time = 0), although this caused a slight cooling of the solutions in the elevated temperature runs. The temperatures of the solutions were determined as each sample was taken; samples taken at more than 2°C below the run temperature (60 or 90°C) were not used in determining the rate constants.

3. RESULTS AND DISCUSSION

3.1 Rate Equations

Oxalic acid [$(COOH)_2$] reacts with hydrogen peroxide to yield CO_2 and water:[5-7]

$$(COOH)_2 + H_2O_2 \xrightarrow{k_1} 2CO_2 + 2H_2O \ . \qquad (1)$$

Hydrogen peroxide is consumed both in reaction (1) and in the acid-catalyzed decomposition reaction

$$H_2O_2 \xrightarrow{k_2} H_2O + 1/2O_2 \ . \qquad (2)$$

The rate equations for the decreases in oxalate and hydrogen peroxide are:

$$d[Ox]/dt = - k_1 [Ox]^n \ [H_2O_2]^m \ , \qquad (3)$$

$$d[H_2O_2]/dt = -k_1 [Ox]^n \ [H_2O_2]^m - k_2 \ [H_2O_2] \ , \qquad (4)$$

where the quantities in square brackets are molar concentrations, Ox is total oxalate, and t is time in hours. Although oxalate can be oxidized by concentrated nitric acid, the rate with the low acid concentrations used in these studies is negligible. The decomposition of hydrogen peroxide is assumed to be the first order with respect to its concentration. In most experiments, the hydrogen peroxide concentration was much larger than the oxalate concentration and could be assumed constant.

3.2 Effect of Oxalate Concentration

Figure 1 is a plot of log oxalate concentration vs time at 90°C for three different initial oxalate concentrations with nearly the same initial hydrogen peroxide concentration. In all cases the concentration changed less than 10% over the duration of the tests. The linearity of the plots indicated that the reaction was first order with respect to the oxalate concentration; hence, n in Eq. (3) is unity.

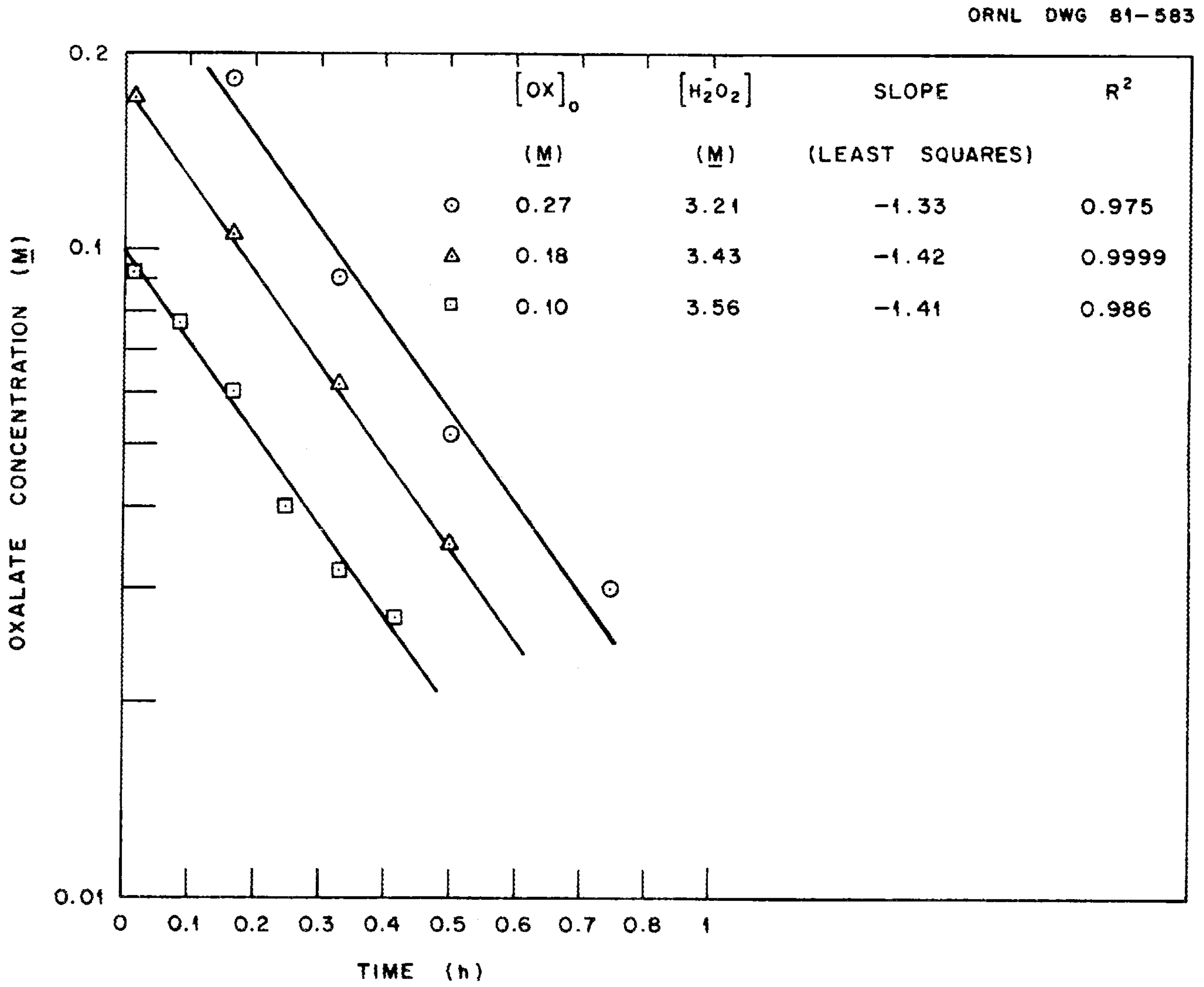

Fig. 1. First order plot for the decrease in oxalate concentration by reaction with hydrogen peroxide.

3.3 Effect of Hydrogen Peroxide Concentration

Equation (3) can be integrated for the conditions of nearly constant hydrogen peroxide concentrations and $n = 1$ to give

$$\ln[\mathrm{Ox}] = - k_1 t\ \overline{[H_2O_2]}^m + \ln\ [\mathrm{Ox}]_0\ ; \tag{5}$$

where $\overline{[H_2O_2]}$ is the average hydrogen peroxide concentration during an experiment and $[\mathrm{Ox}]_0$ is the initial oxalate concentration. In the elevated temperature tests, the oxalate was partially (generally <10%) decomposed at a lower temperature before the experiment had stabilized at the operating temperature. Thus, the initial concentration of oxalic acid added to an experiment has not been used in Eq. (5) but $\ln\ [\mathrm{Ox}]_0$ has been treated as an integration constant.

The effect of the hydrogen peroxide concentration was evaluated by fitting the experimental data ($\ln\ [\mathrm{Ox}]$ vs t) by the least-squares techniques in order to obtain $k_1 \overline{[H_2O_2]}^m$. The value of m was determined by expanding $k_1 [H_2O_2]^m$ in the logarithmic form

$$\log\ k_1 \overline{[H_2O_2]}^m = \log\ k_1 + m\ \log\ \overline{[H_2O_2]}\ ,$$

and plotting $\log\ k_1 \overline{[H_2O_2]}^m$ vs $\log\ \overline{[H_2O_2]}$ (Fig. 2). The slope of the line gave the value for m. The experimental value of m, 0.95, indicated that the reaction was first order with respect to the hydrogen peroxide concentration.

The data of all runs at all temperatures with ~0.3 $\underline{M}$ HNO_3 are summarized in Table 1. The average value of k_1 at 90°C is 0.99 L mol^{-1} h^{-1} with a standard deviation of 0.12. The average values at 60 and 25°C are 0.18 and 0.014 L mol^{-1} h^{-1} respectively.

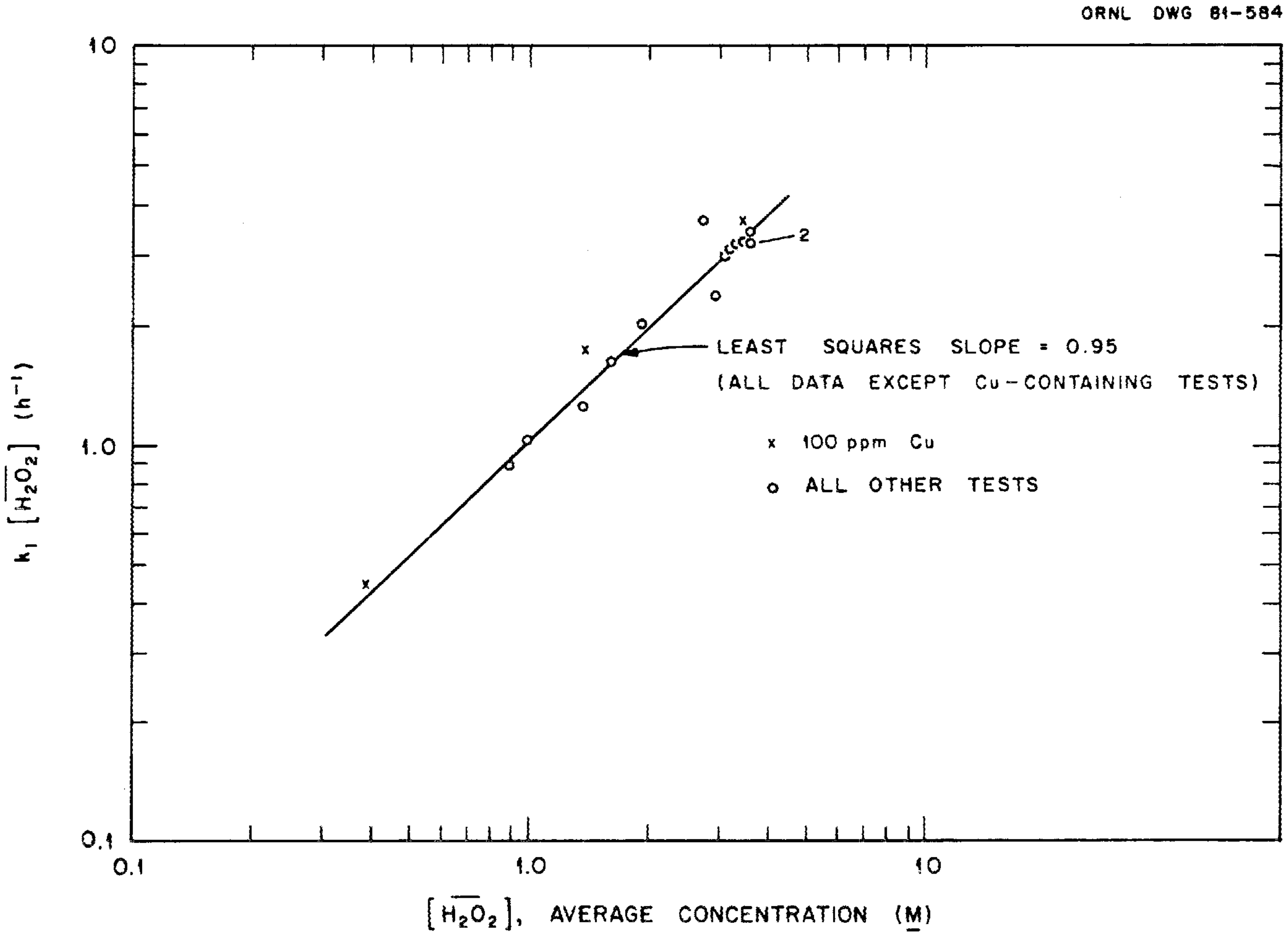

Fig. 2. First order plot for the decrease in hydrogen peroxide concentration by reaction with oxalate.

Table 1. The reaction of hydrogen peroxide with oxalic acid in ~0.27 M HNO_3 solution

Run	Temperature (°C)	$k_1[\overline{H_2O_2}]$ (h^{-1})	Average $[\overline{H_2O_2}]$ (M)	Calculated $[Ox]_0$ (M)	k_1[a] (L mol^{-1} h^{-1})
1	90	3.612	2.76	0.18	1.31
2	90	3.237	3.55	0.17	0.91
3	90	3.267	3.43	0.18	0.95
4	90	1.270	1.37	0.16	0.93
5	90	1.632	1.60	0.17	1.02
6	90	0.886	0.88	0.18	1.00
7	90	1.019	0.98	0.18	1.04
8	90	3.251	3.56	0.098	0.91
9	90	3.434	3.58	0.095	0.96
10	90	2.003	1.91	0.34	1.05
11	90	2.394	2.94	0.28	0.81
12	90	3.053	3.21	0.27	0.95
13	90	1.746	1.39	0.18	1.26[b]
14	90	0.442	0.39	0.18	1.14[b]
15	90	3.676	3.41	0.18	1.08[b]
16	90	3.135	3.24	0.19	0.97[c]
17	90	3.279	3.32	0.19	0.99[c]
17	60	0.55	3.37	0.15	0.16
18	60	0.71	3.42	0.18	0.21
19	25	0.050	3.20	0.17	0.016
20	25	0.037	3.20	0.13	0.012

[a] Correlation coefficients (R^2) $\geq$ 0.97.

[b] Contains 100 ppm copper.

[c] Contains 100 ppm uranium.

3.4 Effect of Added Copper or Uranium

Copper, a known catalyst for peroxide decomposition, was tested in some experimental solutions for possible catalytic effect on the rate of the oxalate-peroxide reaction. The tests with copper at 100 ppm at 90°C (Table 1) gave an average value of k_1 of 1.16 L mol^{-1} h^{-1} with a standard deviation of 0.09; the average value of k_1 in the absence of copper was 0.99 ± 0.12 L mol^{-1} h^{-1}. This indicated that copper might be a slight positive catalyst for the reaction of oxalic acid with hydrogen peroxide. The effect was so small that, even if it existed, it would be insignificant. The presence of 100 ppm uranium had no discernible effect on the rate of the peroxide-oxalate reaction.

3.5 Hydrogen Peroxide Decomposition

The loss of hydrogen peroxide by decomposition in the course of an experiment is measured as the difference between the changes in the total peroxide and oxalate concentrations. The rate constants for the decomposition reaction were calculated from

$$d[H_2O_2]/dt = - k_2 [H_2O_2] \ , \qquad (6)$$

where $[H_2O_2]$ is the peroxide concentration present. Rate constants were calculated for experiments in which the difference between the decreases in the hydrogen peroxide and oxalate concentrations exceeded 0.1 $\underline{M}$; the results are shown in Table 2 for cases with and without copper in the solution. The presence of 100 ppm of copper increased the H_2O_2 decomposition rate constant by about a factor of three in agreement with the known catalytic effect of copper on this decomposition.[8] This method for estimating k_2 is obviously inaccurate since the loss of peroxide by decomposition is small. One test was made to accurately determine the value of k_2 in 0.29 $\underline{M}$ HNO_3 at 90°C; the data are shown in Fig. 3. The rate constant was found to be 0.17 h^{-1} in fair agreement with the 0.12 ± 0.04 h^{-1} found from the oxalate destruction tests (Table 2).

Table 2. Effect of copper on decomposition of hydrogen peroxide

Run	Calculated H_2O_2 loss by decomposition (M)	k_2 (h^{-1})
No copper[a]		
2	0.15	0.092
5	0.14	0.092
6	0.15	0.19
7	0.11	0.12
10	0.20	0.12
100 ppm copper[b]		
13	0.19	0.35
15	0.36	0.36

[a] Average k_2 without copper: 0.12; standard deviation of 0.04.

[b] Average k_2 with 100 ppm copper: 0.36.

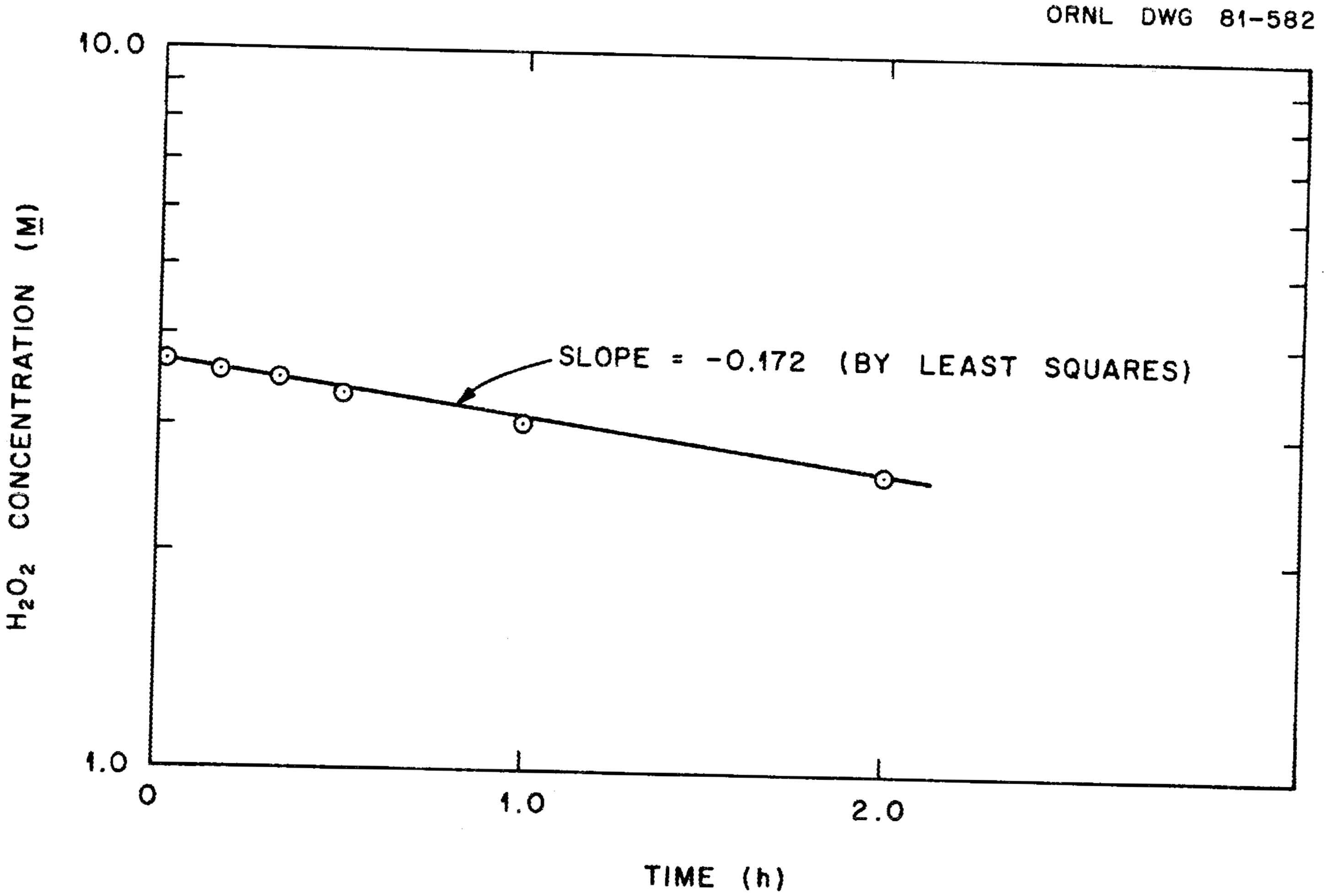

Fig. 3. The decomposition of hydrogen peroxide in 0.29 M HNO_3 solution at the reflux temperature.

3.6 Effect of Hydrogen Ion Concentration

The effect of hydrogen ion concentration on the rate of the reaction of oxalic acid with hydrogen peroxide at 90°C was also studied. The hydrogen ion concentration in the solution of reactants was increased by adding nitric acid or decreased by adding hydrazine. Hydrogen ion activities of the near-neutral solutions were estimated from pH measurements at room temperature because the hydrazine oxalate — hydrogen ion system was considered to be too complex to make a correction for temperature. The data from the low-acid experiments is presented in Table 3; a representative plot of the hydrazine and oxalate concentrations vs time (data of run 2 in Table 3) is shown in Fig. 4.

The hydrogen ion concentrations in the oxalic acid and oxalic acid—nitric acid mixtures were estimated for the reactions at 90°C by the following development. The ionization of oxalic acid occurs in two steps:

$$H_2Ox \rightleftarrows H^+ + HOx^- \quad , \qquad (7)$$

$$HOx^- \rightleftarrows H^+ + Ox^{2-} \quad , \qquad (8)$$

where H_2Ox is un-ionized oxalic acid, HOx^- is the hydrogen oxalate ion, and Ox^{2-} is oxalate ion. The corresponding equilibrium quotients are:

$$K_1 = [H^+][HOx^-]/[H_2Ox] \quad , \qquad (9)$$

$$K_2 = [H^+][Ox^{2-}]/[HOx^-] \quad . \qquad (10)$$

By material balance, the total oxalate, [Ox], is

$$[Ox] = [H_2Ox] + [HOx^-] + [Ox^{2-}] \quad . \qquad (11)$$

In the solutions, two hydrogens originate with each oxalic acid molecule and one with each nitric acid. If the nitric acid is assumed to be completely ionized, the material balance relation for the hydrogen-containing species (equating the hydrogen added to the system to its state at the time being examined) is:

Table 3. The reaction of hydrazine oxalate mixtures with hydrogen peroxide at 90°C

Run	Initial concentrations				k_1	$k_2[H_2O_2]$
	H_2O_2 (M)	Ox (M)[a]	Hydrazine (M)[a]	H^+ (M)[b]	(L mol^{-1} h^{-1})	(mol h^{-1} L^{-1})
1	3.0	0.16	0.33	$\sim 3 \times 10^{-6}$	0.039	0.107
2	3.0	0.26	0.47	$\sim 3 \times 10^{-6}$	0.021	0.038
3	3.0	0.23	0.43	$\sim 2 \times 10^{-7}$	0.018	0.064
4	3.0	0.25	0.44	$\sim 2 \times 10^{-7}$	0.015	0.046
5	3.0	0.21	0.44	$\sim 2 \times 10^{-7}$	0.021	0.073

[a] Estimated from the zero time intercept of the least-squares fit of log [Ox] or log [hydrazine] vs time plot (see Fig. 4).

[b] From pH measurements at room temperature.

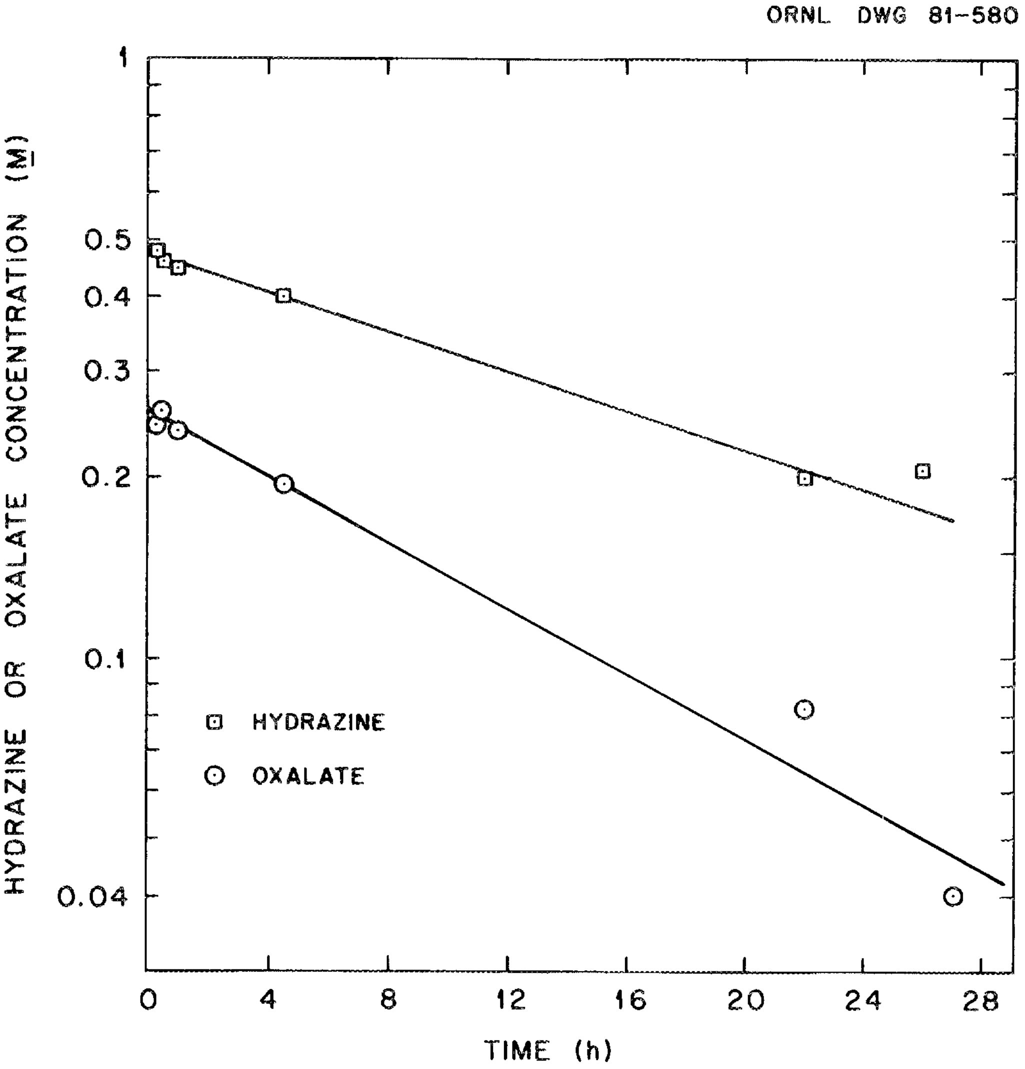

Fig. 4. The reaction of hydrazine and oxalate (aqueous hydrazine oxalate solution) with 3 M H_2O_2 at 90°C and ~3 x 10^{-6} M H^+.

$$[HNO_3] + 2[Ox] = [H^+] + [HOx^-] + 2[H_2Ox] \ . \tag{12}$$

This can be rearranged to

$$[H^+] = [HNO_3] + 2[Ox] - [HOx^-] - 2[H_2Ox] \ . \tag{13}$$

Solving Eq. (9) for $[HOx^-]$ gives

$$[HOx^-] = K_1 [H_2Ox]/[H^+] \ . \tag{14}$$

Solving Eq. (10) for $[Ox^{2-}]$ and substituting Eq. (14) gives

$$[Ox^{2-}] = K_1 K_2 [H_2Ox]/[H^+]^2 \ . \tag{15}$$

Substituting Eqs. (14) and (15) into Eq. (11) and Eq. (14) into Eq. (13) gives

$$[Ox] = [H_2Ox] \left\{1 + \frac{K_1}{[H^+]} + \frac{K_1 K_2}{[H^+]^2}\right\} , \tag{16}$$

$$[H^+] = [HNO_3] + 2[Ox] - [H_2Ox] \left\{\frac{K_1}{[H^+]} + 2\right\} \ . \tag{17}$$

Solving Eqs. (16) and (17) for $[H_2Ox]$ and equating gives

$$\frac{[Ox]}{\left\{1 + \frac{K_1}{[H^+]} + \frac{K_1 K_2}{[H^+]^2}\right\}} = \frac{[HNO_3] + 2[Ox] - [H^+]}{\left\{\frac{K_1}{[H^+]} + 2\right\}} = [H_2Ox] \ . \tag{18}$$

Equation (18) can be solved for $[H^+]$ by trial and error and the effect of hydrogen ion on the oxalate-peroxide reaction can be determined.

Since K_1 and K_2, the first and second dissociation constants of oxalic acid, in Eq. (18) are temperature-dependent, those quantities were estimated at 90°C from the literature values of K_1 and K_2 reported for temperatures up to 45 and 50°C respectively.[9,10] That type of data is usually correlated by equations of the form

$$\log K = -A^*/T + D^* - C^*T, \qquad (19)$$

where A*, D*, and C* are constants, and T is the temperature in kelvin.

The K_1 values for temperatures ≤ 45°C are contained in Table 4.

Table 4. Effect of temperature on K_1 (Ref. 11)

t(°C)	K_1	$\log K_1$
0	0.05702	-1.244
15	0.05598	-1.252
25	0.05598	-1.252
35	0.05176	-1.286
45	0.05070	-1.295

These data are correlated by

$$\log K_1 = -690.14/T + 3.7867 - 0.0091564/T \ (\pm 0.009 \text{ on } \log K_1)^{\ddagger} . \qquad (20)$$

The correlation equation for the variation of K_2 with temperature is

$$\log K_2 = -1539.3/T + 7.1966 - 0.0212\ T \ (\pm 0.001 \text{ on } \log K_2) . \qquad (21)$$

The estimated values of K_1 and K_2 at 90°C using Eqs. (20) and (21) are 3.6×10^{-2} and 1.815×10^{-5} respectively. Since the changes in K_1 and K_2 with temperature are moderate, this extrapolation beyond the temperature range of the data is probably acceptable. In addition, the average of the initial and final oxalate concentrations, $\bar{\Sigma}$[Ox], was used for [Ox] in Eq. (18) because the oxalate concentration decreased during the experiment. The results of the calculations of hydrogen ion concentrations for the higher acidity are given in Table 5.

The effect of the hydrogen ion concentration, $[H^+]$, on the reaction rate was determined from a plot of $\log k_1$ vs $\log [H^+]$ (Fig. 5) using the results contained in Tables 3 and 5. The data were well correlated by a line of slope 0.3 from ~2×10^{-7} to 0.538 M in hydrogen ion. The small

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‡R^2 (correlation coefficient) = 0.92.

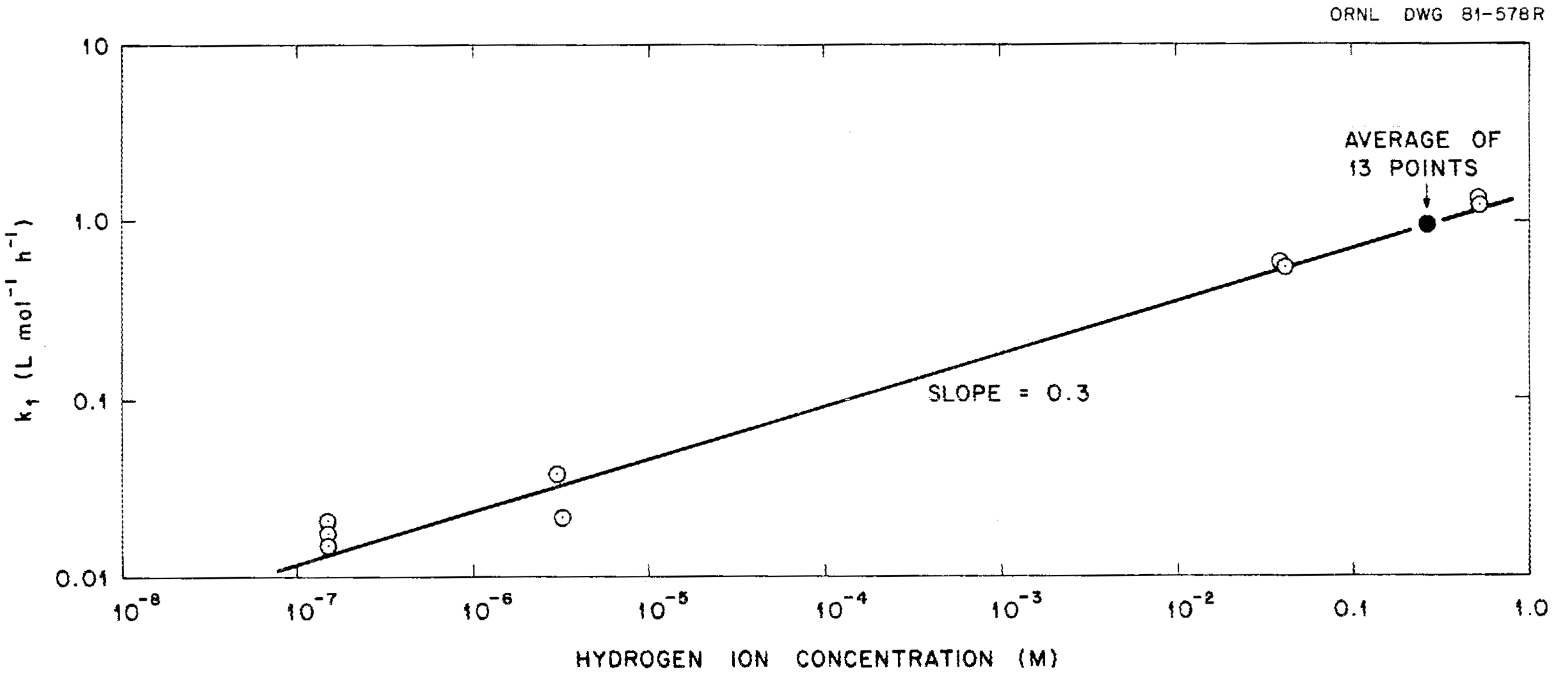

Fig. 5. The effect of hydrogen ion concentration on k_1 at 90°C.

Table 5. Calculated values of the hydrogen ion concentration at 90°C

Run	HNO_3 (M)	$\overline{\Sigma}Ox$[a] (M)	$[H^+]$ (M)
1	0.29	0.095	0.301
2	0.26	0.096	0.272
3	0.26	0.102	0.273
4	0.26	0.106	0.273
5	0.26	0.108	0.273
6	0.26	0.128	0.275
7	0.28	0.118	0.294
8	0.26	0.06	0.268
9	0.265	0.06	0.273
10	0.26	0.176	0.281
11	0.26	0.12	0.275
12	0.26	0.106	0.273
16	0.25	0.078	0.26
17	0.26	0.074	0.269
21	0.537	0.088	0.543
22	0.538	0.09	0.544
23	0	0.078	0.039
24	0	0.094	0.043

[a] Average total oxalate concentration.

effect of the hydrogen ion concentration suggested that hydrogen ion did not participate directly in the reaction between oxalate and hydrogen peroxide. A possible explanation might be that oxalic acid (H_2Ox), hydrogen oxalate ion (HOx^-) and oxalate ion (Ox^{2-}) reacted with hydrogen peroxide at different rates so that changes in the reaction rates with hydrogen ion concentration reflected shifts in the distribution of various oxalate species. However, sufficient data was not available to prove this hypothesis.

Rate constants for the disappearance of hydrazine from near-neutral solutions by reaction with hydrogen peroxide, $k_2[H_2O_2]^p$, are included in Table 3. The exponent p is an unknown power effect for the hydrogen peroxide concentration on the reaction rate. The slow reaction rate indicated that the destruction of hydrazine by hydrogen peroxide under these conditions was not an acceptable process option. The reaction is known to proceed with fair rapidity in basic solutions, but the rate decreases as the pH decreases.[11]

3.7 Effect of Temperature

The effect of temperature on the rate of the reaction of oxalate with hydrogen peroxide in ~0.3 M HNO_3 solution was determined from a plot of log k_1 vs 1/K (Fig. 6). The activation energy for the reaction, calculated from the slope of the line fitted to the data by the method of least squares, is 57.8 kJ/g-mol (13.82 kcal/g-mole). This result was used in an empirical equation [Eq. (22)] which related the disappearance of oxalate to the temperature and included the effects of hydrogen ion and hydrogen peroxide concentrations,

$$\ln([Ox]/[Ox]_0) = -2.98 \times 10^8\ t\ [H^+]^{0.3}\ [\overline{H_2O_2}]\ \exp -(13{,}820/1.987\ K). \quad (22)$$

The average value of the hydrogen peroxide concentration, $[\overline{H_2O_2}]$, is used because the change in concentration is small.

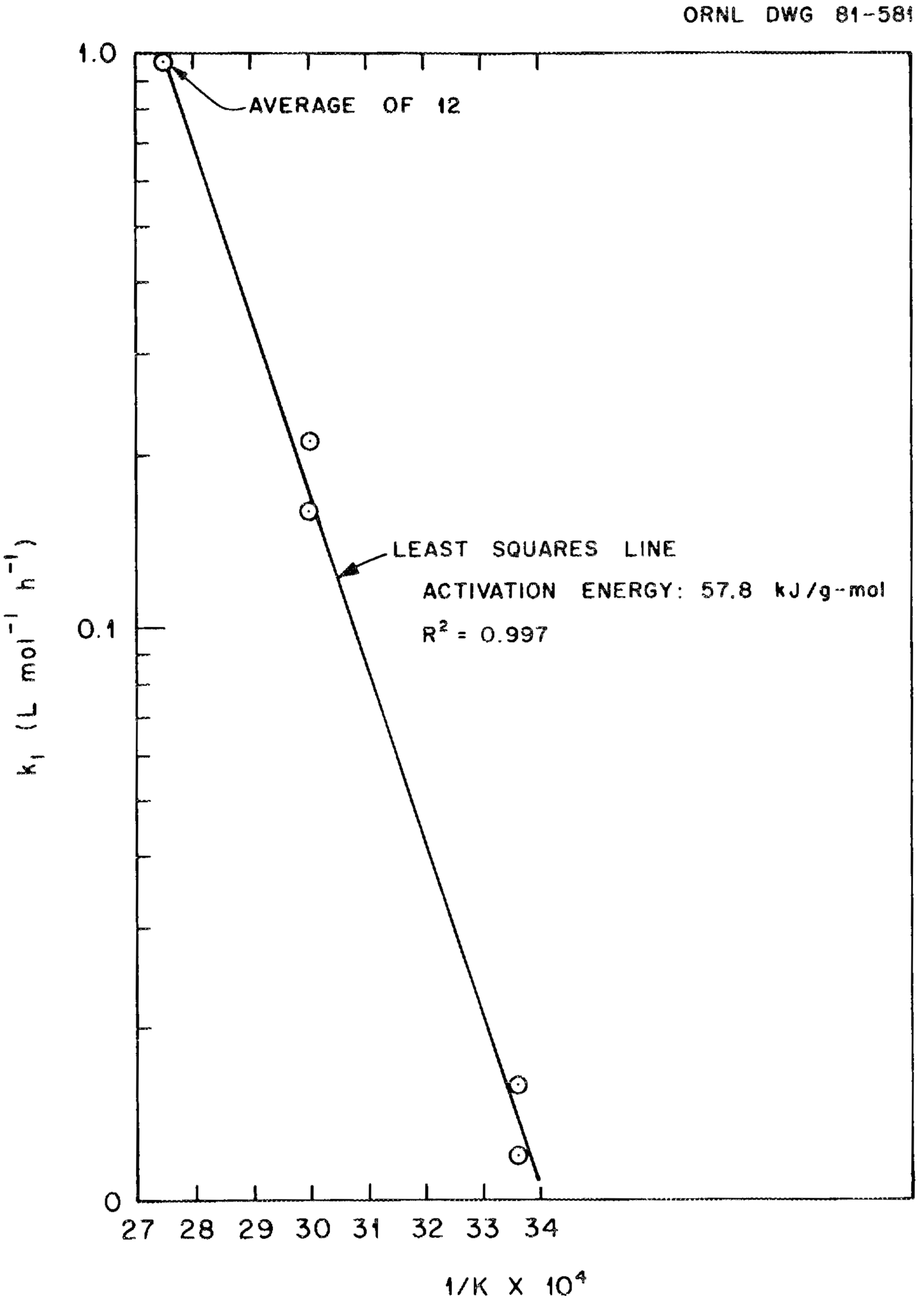

Fig. 6. The activation energy of the reaction of oxalate with hydrogen peroxide.

3.8 Tests of the Kinetic Model

The proposed kinetic model for the destruction of oxalate by reaction with hydrogen peroxide was tested by comparing the measured and calculated results for an experiment in which the initial hydrogen peroxide concentration was about five times the initial oxalate concentration (Table 1, run 6). The experimental results are plotted as the logarithms of the oxalate and hydrogen peroxide concentrations vs time (Fig. 7); both plots exhibit distinct curvatures. The theoretical curves in the same figure were prepared from data on the reactant concentrations calculated by use of the equations of the kinetic model, Eqs. (3) and (4), with m and n equal to unity and with values for k_1 and k_2 at 90°C of 1.0 L mol^{-1} h^{-1} and 0.19 h^{-1} respectively. The excellent agreement between the two sets of results is a verification of the proposed kinetic model.

3.9 Oxalate Destruction at Process Conditions

For process application, it is probable that the oxalate would be disposed of by reaction with hydrogen peroxide in 0.3 $\underline{M}$ HNO_3 solution at the reflux temperature, about 100°C. The oxalate concentration can be calculated as a function of time for process conditions by Eq. (23) if the values of k_1 and m, 1.67 L mol^{-1} h^{-1} at 100°C and unity, respectively, are inserted in Eq. (5) and if the hydrogen peroxide concentration is almost constant,

$$\ln ([Ox]/[Ox]_0) = -1.67\ t\ \overline{[H_2O_2]}\ . \qquad (23)$$

Further substitution and rearrangement of Eq. (23) leads to the relation for the half-time, t(0.5), for oxalate destruction, Eq. (24),

$$t(0.5) = 0.415/\overline{[H_2O_2]}\ . \qquad (24)$$

Representative half-times for oxalate in about 0.3 $\underline{M}$ HNO_3 at 100°C are:

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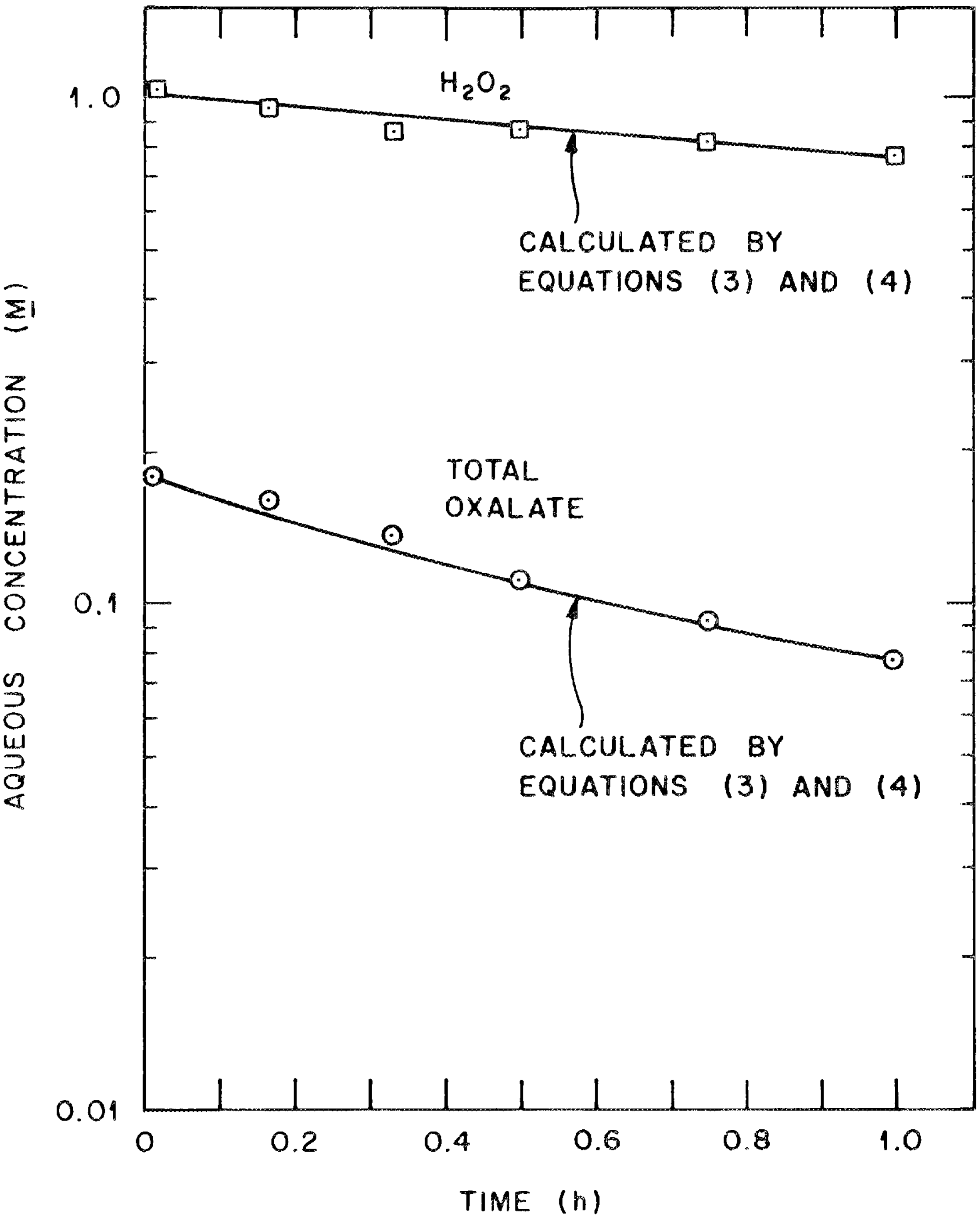

Fig. 7. A test of the kinetic model at 90°C in 0.26 M HNO_3 solution.

$[H_2O_2]$ M	t(0.5) (h)
0.1	4.2
0.5	0.8
1	0.4
1.5	0.3
2.0	0.2

The half-times should be short enough for use in a process for oxalate destruction with hydrogen peroxide concentrations greater than 0.5 M. The rates of destruction will be increased in more acidic solutions (Sect. 3.7).

4. CONCLUSIONS

The rate of destruction of oxalate by oxidation with hydrogen peroxide in acid solution at the reflux temperature would be adequate for process application. Calculated reaction half-times at 100°C would be less than 1 h when the hydrogen peroxide concentration was greater than 0.5 M (about 1.5 wt %). The reaction was first order with respect to both the oxalate and hydrogen peroxide concentrations and had an activation energy of 58.7 kJ/g-mol. The rate increased with the hydrogen ion concentration as $[H^+]^{0.3}$ but was not significantly affected by the presence of 100 ppm of copper or uranium in solution. In the near-neutral hydrazine oxalate solutions, the reaction of either component with hydrogen peroxide is very slow; therefore, their simultaneous destruction is not feasible in processing applications. A better scheme would be the destruction of hydrazine by nitrous acid in acidic solution followed by the destruction of oxalate by hydrogen peroxide. Alternatively, the oxalate could be destroyed by reaction with concentrated nitric acid.

5.0 ACKNOWLEDGMENTS

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