[CONTRIBUTION FROM THE METCALF CHEMICAL LABORATORIES OF BROWN UNIVERSITY]

The Mechanism of the Oxidation of 2-Propanol by Peroxydisulfate Ion

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A reinvestigation of the kinetics and mechanism of the aqueous peroxydisulfate oxidation of 2-propanol has been carried out by two different experimental techniques. The direct interaction of the reagents can be studied only after oxygen inhibition and trace metal catalysis are eliminated. Mechanistic pathways for the reaction are discussed, and free radical chain sequences consistent with the data are presented.

The kinetics of the oxidation of alcohols by peroxydisulfate ion have been studied several times[2-5] but the results have not led to a satisfactory understanding of the reaction mechanism. In order to clarify the points of disagreement to be found in the literature and particularly to test the mechanisms postulated by Levitt[4,6] the present studies[1] were carried out, primarily on 2-propanol as the reductant.

EXPERIMENTAL

Materials. Two samples of 2-propanol were used with identical results. One sample, Eastman Spectro-Grade, was used without purification; the other, Union Carbide and Carbon 99%, was purified by refluxing over calcium oxide followed by distillation. The potassium peroxydisulfate, B & A Reagent Special Grade, was initially used without purification; careful recrystallization from conductivity water caused a significant decrease in rate (see below). Other materials including Na_2H_2Y (the disodium salt of ethylenediaminetetracetic acid) were best grade available and were used without further purification. The early experiments were carried out with good quality distilled water; some later experiments were run with conductivity water.

Titration runs. Two methods for following the reaction were employed. The first method was by iodometric analysis of unchanged peroxydisulfate. As the reaction proceeds at a convenient rate, standard procedures for pipetting and analyzing aliquots were employed.

Spectrophotometric runs. Because of several difficulties (nonlinear plots, oxygen interference, catastrophes, etc.) which will be discussed below, it was desirable to find an alternative method for following the kinetics of this reaction. A spectrophotometric method was developed which involved the continuous measurement of absorbance at 2725 Å versus time with the Beckman DK-1 Recording Spectrophotometer. This wavelength was picked to give maximum change in absorbance during the course of a run. Acetone has a broad, rather weak absorption band centered at 2640 Å, while peroxydisulfate absorbs in a continuum from about 3600 Å out to beyond 2000 Å. With an initial peroxide concentration of 0.05*M* and a five-fold excess of alcohol (nonabsorbing) a change in absorbance ($A = \log I_0/I$) from about 0.45 to 0.90 was obtained over the course of the entire reaction. Normally the recorder was run at a chart speed of 0.5 inches per min. However, it was possible to interrupt a kinetic run at any point and rapidly scan the entire ultraviolet spectrum.

The early spectrophotometric experiments were made using a phosphate-sulfate buffer of *p*H 8.0 and ionic strength 0.5 as Levitt and Malinowski[4] had done. Comparable results were obtained, however, if the reaction were run in distilled water; thus the buffer was not employed in later runs. In all cases the reference solution was of the same composition as the reacting solution, with the omission of the peroxydisulfate. Matched ground-glass stoppered silica cells of 10-mm. path length were employed.

In the runs in which it was desired to exclude oxygen, the peroxide solution was saturated with nitrogen gas by bubbling the solution at 25° in an external Pyrex vessel for 2 hr. This 250-ml. vessel was equipped with a condenser jacket through which water from a constant temperature bath could be circulated to bring the solution up to temperature prior to the beginning of the run. The calculated amount of alcohol was added through a self-sealing rubber stopper with a hypodermic syringe at zero time and the solution rapidly mixed with a magnetic stirrer. The solution was then pumped under nitrogen into the spectrophotometer cell, which was equipped with a ground-glass adapter, allowing the cell to be thoroughly rinsed by several cell volumes of the reacting solution and filled without contacting the air. The solution remaining in the external vessel was used to follow the kinetics simultaneously by iodometric titration.

Temperatures within the spectrophotometer were maintained to ±0.5° by means of a thermostated cell holder through which constant temperature water was circulated. The entire mixing and transfer procedure took less than 1 min. A similar procedure was followed for the runs made in solutions saturated with oxygen. When the exclusion of air was not required, the solution of peroxydisulfate was allowed to come to temperature in the cell in the spectrophotometer. Alcohol was then added directly to the cell from a micropipette and the solution mixed by shaking; this procedure required about 15 seconds.

RESULTS

Stoichiometry. Yields of 88 ± 3% of acetone were isolated from the 2-propanol oxidation by precipitation of the ketone as its 2,4-dinitrophenylhydrazone. No other organic product could be found. In the ultraviolet spectra, an isosbestic point at 2570 Å persisted throughout the course of the reaction. Within the experimental error of the spectral method (0.01 absorbance units, or about ±2%), this plus the change in absorbance at 2725 Å confirm the stoichiometry of the reaction as

$$S_2O_8^{--} + R_2CHOH \longrightarrow 2SO_4^{--} + R_2CO + 2H^+$$

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[1] (a) Ph.D. Thesis at Brown University (1956). (b) Ph.D. Thesis at Brown University (1960).

[2] P. D. Bartlett and J. D. Cotman, *J. Am. Chem. Soc.*, **71**, 1419 (1949).

[3] I. M. Kolthoff, E. J. Meehan, and E. M. Carr, *J. Am. Chem. Soc.*, **75**, 1439 (1953).

[4] L. S. Levitt and E. R. Malinowski, *J. Am. Chem. Soc.*, **77**, 4517 (1955); **78** 2018 (1956); **80** 5334 (1958).

[5] K. B. Wiberg, *J. Am. Chem. Soc.*, **81** 252 (1959).

[6] (a) L. S. Levitt, *Can. J. Chem.*, **31** 915 (1953); (b) L. S. Levitt, *J. Org. Chem.*, **20**, 1297 (1955).

TABLE I

SUMMARY OF TITRATION DATA ON THE PEROXYDISULFATE OXIDATION OF 2-PROPANOL AT 40°

*p*H	μ	[P(V)][a]	$[Na_2H_2Y]$	$[SO_4^{--}]_0$	$[R_2CHOH]_0$	$[S_2O_8^{--}]_0$	k, min.$^{-1}$
8	0.5	0.05*M*	0	0.10*M*	0.05*M*	0.02*M*	1.5×10^{-3}[b]
8	1.5	0.5	0	0	0.02	0.02	—
8	1.5	0.5	0	0	0.42	0.02	0.5×10^{-3}
3–2	0.06	0	0	0	0.42	0.02	1.0×10^{-3}
3–2	0.06	0	0	0	0.42	0.02	1.0×10^{-3}
3–2	0.06	0	0	0	0.42	0.02	0.5×10^{-3}
3–2	0.06	0	0	0	0.83	0.02	0.7×10^{-3}
8	1.5	0.5	$4 \times 10^{-4}M$	0	0.42	0.02	[c]
3	0.06	0	4×10^{-4}	0	0.42	0.02	[c]

[a] Concentration of total phosphate. [b] Value predicted by the data of Levitt and Malinowski.[4] [c] Observed decrease in $[S_2O_8^{--}]$ did not exceed the usual experimental error in the course of six hours. See text.

where R_2CHOH signifies 2-propanol and R_2CO signifies acetone.

Titration runs. A summary of kinetic experiments at 40° are presented in Table I. Generally the reaction was followed over the course of one half-life, and in such cases the reaction appeared to be first order in peroxydisulfate concentration. However, in runs carried over more than one half-life, the first order plots showed a small but significant sigmoid-shaped wiggle about the best straight line; this curvature, which was definitely outside the experimental error and will be mentioned later, is an indication of a complicated mechanism.

The possible effect of *p*H on the reaction was studied. Runs were made in solutions buffered by phosphate at *p*H 8 and in unbuffered solutions, in which the *p*H generally varied from 3 to 2 in the course of one half-life. Although there was a fairly wide variation (0.5×10^{-3} to 1×10^{-3} min.$^{-1}$) in the values of the apparent first order rate constants at 40°, no significant dependence on *p*H exists for the observed first order oxidation.

In their original study of the oxidation at 60°, Levitt and Malinowski[4] used an initial concentration of 0.02*M* for $S_2O_8^{--}$ and varied the initial concentration of R_2CHOH from 0 to 0.2*M;* a limiting first order rate was observed using an initial concentration of 0.05*M* for R_2CHOH. In the present titration study at 40°, the initial concentration of $S_2O_8^{--}$ was always 0.02*M*. When an initial concentration of 0.02*M* was used for R_2CHOH, there was no apparent reaction. No significant variation in the observed first order rate constant occurred when the initial concentration of R_2CHOH was varied from 0.42 to 0.83*M*.

A significant result of these data is the fact that the observed first order rate constants at 40° were sometimes less than the value predicted by Levitt and Malinowski (obtained using their observed value of 1.05 hr.$^{-1}$ for the limiting first order rate constant at 60° and their reported value of 26 kcal./mole for the Arrhenius activation energy). The kinetic studies of Levitt and Malinowski were made using reaction solutions containing rather large amounts (0.1*M*) of sulfate ion, to which those authors ascribed an inhibiting effect on the rate of the oxidation. The fact that slower rates were observed in the present study, even though no sulfate ion was added to the reaction solutions, is particularly noteworthy. Also, in the presence of small amounts ($4 \times 10^{-4}M$) of the powerful sequestering agent Na_2H_2Y the observed rate was markedly reduced; there was no apparent reaction during time intervals comparable to the time of one half-life in the absence of Na_2H_2Y.

In Fig. 1, data on the oxidation of three alcohols by peroxydisulfate ion are shown. Before the addition of Na_2H_2Y (shown by vertical bars) all three rates are identical within the experimental error; the first order rate constants are 2.1×10^{-3}, 1.9×10^{-3}, and 2.0×10^{-3} in units of min.$^{-1}$ for methanol, ethanol, and 2-propanol respectively. Also, these rates are not the same as those presented in Table I, for a different batch of buffer was employed. Although the rates after addition of Na_2H_2Y were too slow to be determined accurately, all three reactions are inhibited in the same way and to a similar degree by this sequestering agent.

Additional data, which were obtained at 50°, are presented in Table II; the results are similar to those obtained at 40°. It was observed, however, that the peroxydisulfate ion reacts with Na_2H_2Y. At 50° in solutions buffered at *p*H 8, about 5% of the peroxydisulfate (in the absence of alcohol) reacted during the first three hours of the run; subsequently, the observed first order rate slowed down to a value equal to that observed in the absence of Na_2H_2Y. The first order rate constant (k = *ca.* 0.8×10^{-4} min.$^{-1}$), observed at 50° at *p*H 8 in the absence of Na_2H_2Y, compares favorably with the value reported by Kolthoff and Miller[7] ($k = 0.87 \times 10^{-4}$ min.$^{-1}$ at *p*H 7 and at 50°) for the oxidation of water by peroxydisulfate ion. The rate of this oxidation has been shown[7] not to be explicitly dependent on *p*H (except in strong acid) or ionic strength. Returning to the peroxydisulfate reaction with Na_2H_2Y, the initial concentration of Na_2H_2Y was 0.0006*M* compared with 0.02*M* for $S_2O_8^{--}$; it is suggested that two peroxydisulfate

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[7] I. M. Kolthoff and I. K. Miller, *J. Am. Chem. Soc.*, **73**, 3055 (1951).

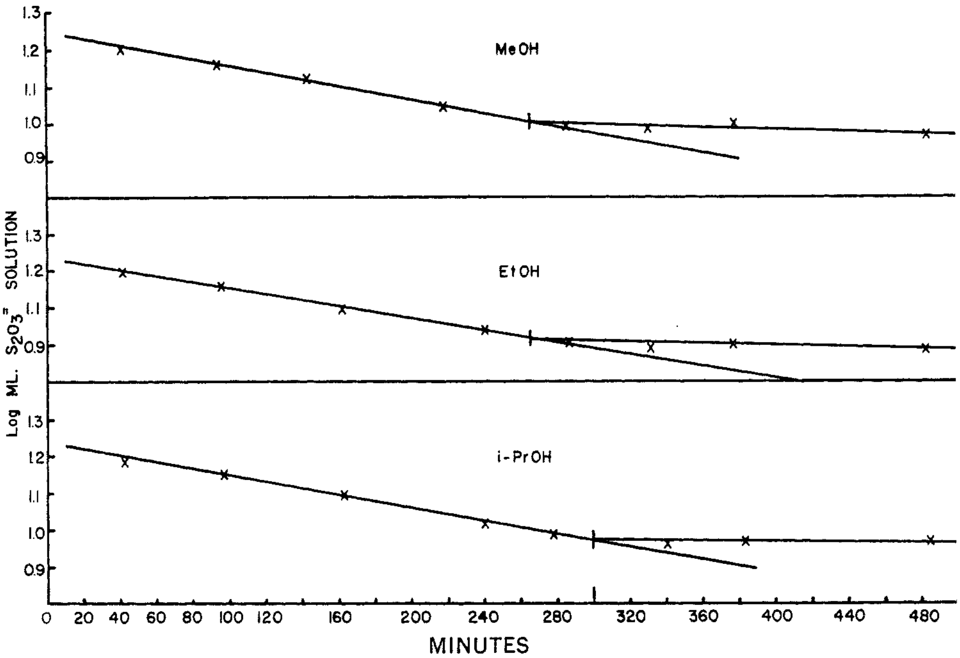

Fig. 1. Results obtained by the titration method for the oxidation of three alcohols (methanol, ethanol, and 2-propanol) by peroxydisulfate ion at 50°. The vertical bar indicates the point of addition of complexing agent

ions reacted with one molecule of Na_2H_2Y. Possibly oxidation occurs at the two amino nitrogens of the Na_2H_2Y molecule[8]

At pH 8 in phosphate buffer, which contains no Na_2H_2Y, $S_2O_8^{--}$ oxidizes R_2CHOH rapidly. The oxidation appears to be first order in the concentration of $S_2O_8^{--}$. A value of 2.0×10^{-3} min.$^{-1}$ for the first order rate constant was observed for the oxidation in the absence of Na_2H_2Y; the value for k predicted by the results of Levitt and Malinowski is 5.3×10^{-3} min.$^{-1}$

In the presence of Na_2H_2Y ($6 \times 10^{-4}M$), the oxidation proceeded slowly at first. These initial portions of the runs were plotted as first order in the concentration of $S_2O_8^{--}$ and the apparent rate constants listed in Table II. Variations in the initial concentration of R_2CHOH from 0.22 to $0.88M$ produced no apparent change in the indicated rate constant. However, after the passage of from three to six hours, a relatively rapid decrease (*ca.* $5 \times 10^{-3}M$) in the concentration of $S_2O_8^{--}$ occurred. Subsequently, the oxidation readopted an apparent first order behavior, but the reaction was somewhat less rapid than before the "catastrophe." Subsequent experiments, described below, revealed the cause of this behavior as interaction of dissolved oxygen with reaction intermediates.

Spectrophotometric data. The problem of the presentation of the experimental data obtained with the spectrophotometer is somewhat complicated by the complexity of the reaction. For this reason, the various factors affecting the reaction are discussed below in an order which attempts to be systematic (rather than chronological). Pertinent tables of data are included as needed. A complete summary of the experimental runs is given elsewhere.[1b]

Effect of oxygen. The most striking result obtained was the observation of a definite inhibition period, the length of which depended on the amount of dissolved oxygen present in the solution. When the solution was rigorously deprived of oxygen, a quite rapid reaction was observed which appeared pseudo-first-order in persulfate in the presence of a large excess of alcohol. When the reaction was run in the closed cell with solution which had been in equilibrium with the air, a much slower reaction with a rate which remained apparently constant was observed for a reproducible period of time lasting from 3 to 124 minutes (depending on conditions). At the end of this inhibition period there was a sudden significant increase in rate to the value found in the absence of oxygen, and pseudo-first-order kinetics ensued and continued until the completion of the reaction. When the reaction was run in a solution saturated with oxygen, the inhibition period continued until the persulfate was exhausted although after about one half-life the rate slowed down and approached higher order kinetics before completion. Spectrophotometer plots for these three cases in buffered solution at 60° are shown in Fig. 2. It is obvious from these results that at least two separate reactions are involved. For simplicity of discussion the slow, initial reaction involving oxygen will be called reaction A; and the rapid reaction which takes place in the absence of oxygen

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(8) N. M. Beileryan, *Nauch. Trudy Erevan. Gosudarst. Univ. Ser. Khim. Nauk*, **60**, 143 (1957); *Chem. Abstr.*, **53** 11081 (1959).

TABLE II

SUMMARY OF TITRATION DATA ON THE PEROXYDISULFATE OXIDATION OF 2-PROPANOL AT 50°

*p*H	μ	[P(V)][a]	[Na_2H_2Y]	[SO_4^{--}]$_0$	[R_2CHOH]$_0$	[$S_2O_8^{--}$]$_0$	k, min.$^{-1}$ $\times 10^3$
7	0.13	ca.0.04M	0	0	0	0.01M	0.087[b]
10	0.13	0	0	0	0	0.01	0.068[b]
8	1.5	0.5	0	0	0	0.02	ca. 0.08
8	1.5	0.5	0	0	0	0.02	ca. 0.08
8	0.5	0.05	0	0.1M	0.05	0.02	5.3[c]
8	1.5	0.5	0	0	0.42	0.02	2.0
8	1.5	0.5	$6 \times 10^{-4}M$	0	0.22	0.02	0.38
8	1.5	0.5	6	0	0.42	0.02	0.53
8	1.5	0.5	6	0	0.42	0.02	0.42
8	1.5	0.5	6	0	0.42	0.02	0.42
8	1.5	0.5	6	0	0.88	0.02	0.38
8	1.5	0.5	6×10^{-5}	0	0.05	0.02	0.38

[a] Concentration of total phosphate. [b] Data obtained by Kolthoff and Miller[7]; carbonate buffer used at *p*H 10. [c] Value predicted by data of Levitt and Malinowski.[4]

will be referred to as reaction B. The sudden transition from A to B apparently corresponds to the exhaustion of dissolved oxygen. After reaction B had begun, simply removing the stopper from the spectrophotometer cell for a second to admit air, followed by brief shaking, was sufficient to stop B and cause the rate of A to be reassumed.

The catastrophies found in the titration experiments can be explained as the rapid increase in rate observed *at the transition from reaction A to* B upon the exhaustion of dissolved oxygen. This sudden transition is quite striking on the continuous curves obtained from the spectrophotometer. In the runs with distilled water this transition is even more sharp than for the buffered solution, although it was observed in both cases. The catastrophies were observed (as discontinuous gaps in the titration data) only when EDTA was present, as under these conditions the rate of disappearance of persulfate was sufficiently reduced for dissolved oxygen to become exhausted between infrequent titrations. This was possible as, even though EDTA greatly decreased the rate of loss of persulfate during reaction A, it did not significantly affect the length of time required to exhaust the dissolved oxygen (see Table III). The implications of this observation will be considered later.

TABLE III

THE EFFECT OF VARIOUS INHIBITORS ON REACTION RATES

Added Substance[a]	R(A)[b]	τ(A)[c]	$k_{3/2}$(B)[d]
None	1.8×10^{-3}	5.5	0.96
Triethylamine	2.0×10^{-3}	5.8	0.85
Triethylamine and acetic acid	2.2×10^{-3}	5.3	0.86
EDTA	0.40×10^{-3}	5.3	0.86
EDTA	0.50×10^{-3}	5.5	1.00
None[e]	0.59×10^{-3}	5.3	0.87

[$S_2O_8^{--}$]$_0$ = 0.049M; [R_2CHOH]$_0$ = 0.39M; 60.0°; unbuffered solution

[a] Concentration = $10^{-5}M$. [b] Initial rate of reaction A in moles/l.$^{-1}$/min.$^{-1}$ [c] Inhibition period in minutes. [d] Rate of reaction B in l.$^{1/2}$/mole$^{-1/2}$/min.$^{-1}$ [e] Recrystallized potassium peroxydisulfate in de-ionized water.

Comparison of methods. It is known that persulfate ion can decompose by a photochemical reaction to produce radicals, as well as by a thermal process.[9] In order to show that photochemical decomposition was not responsible for the complex kinetics observed in the spectrophotometer, the kinetics of the reaction in several runs were followed simultaneously by iodometric titrations of the solution remaining in the external thermostated cell. Care was taken to minimize the introduction of oxygen during sampling. Curves showing the results obtained by the two methods are given in Fig. 3. The curves labeled I were obtained from the same solution, in the presence of an excess of oxygen. The curves labeled II were obtained from another solution, which had been purged of most of its dissolved oxygen with nitrogen gas. Notice *that the transition from reaction A to reaction B* occurs at the same time in the external sample as in the sample receiving ultraviolet radiation in the spectrophotometer. Slight differences in the concentrations detected by the two methods are to be expected, as quenching of the reaction solution for the titrations was insufficiently fast compared to the rate of the fast reaction B. Also, despite precautions, oxygen seems to have been introduced into the titration experiment before completion. It is obvious, however, that the same major kinetic process is being monitored in both cases, and that the effects observed are not due to photochemical initiation of persulfate decomposition within the spectrophotometer.

From the comparison discussed in this section and from the results shown in Figs. 2 and 3, one definite conclusion can be drawn. The rates observed in the titration experiments were (excepting, of course, the catastrophies) those for reaction A. Therefore, the conclusions drawn from the results

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(9) M. S. Tsao and W. K. Wilmarth, *J. Phys. Chem.*, **63**, 346 (1959).

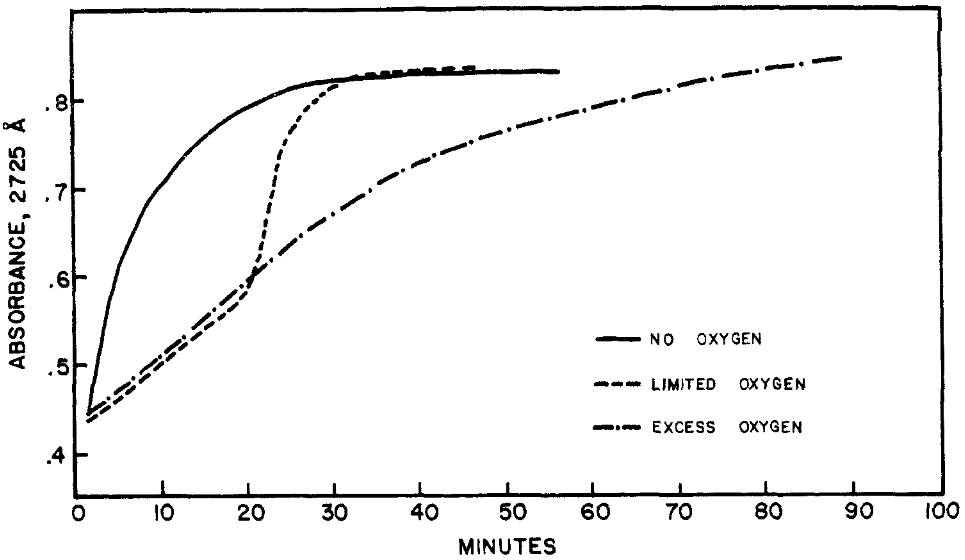

Fig. 2. Plots of absorbance at 2725 Å versus time for three runs with different initial amounts of dissolved oxygen at 60° in buffered solution

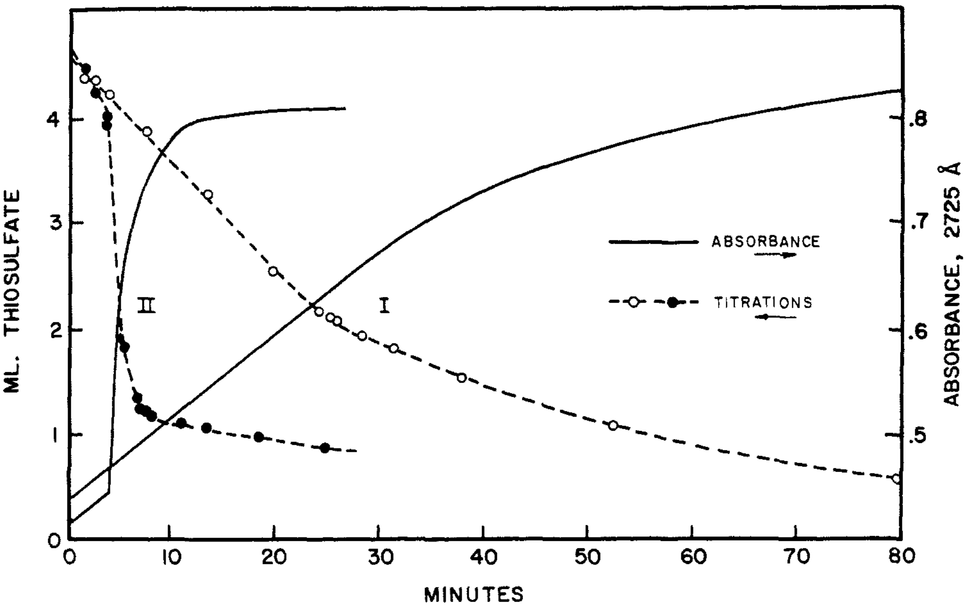

Fig. 3. Kinetic experiments to demonstrate that the two analytical methods give comparable results

of titration runs may be carried over to the sections below dealing with reaction A.

Reaction A orders. Reaction A is observed only in the presence of dissolved oxygen gas. A plot of absorbance *vs.* time is linear over as much as one half-life (see Fig. 2), making the reaction appear initially zero order in all reactants. At longer reaction time, however, the reaction slows down, approaching higher order kinetics. By varying the initial concentration of each component, the reaction was zero order in alcohol and zero order in oxygen, but not zero order in persulfate. The initially constant rate *vs.* time is then an indication of a complex reaction.

The usable absorbance range of the spectrophotometer so limited the range over which the initial persulfate concentration could be varied that it was difficult to define definitely the order with respect to persulfate concentration by this method. As mentioned earlier, if the titration data for the reaction A are plotted as first order (see Fig. 4), the resulting curve, which is reasonably fitted by the dotted straight line, actually has a soft sigmoid shape. This sigmoid shape was observed in spectrophotometric runs as well as titration runs. The spectrophotometric method, by providing a continuous curve rather than scattered points, emphasizes the deviations from linearity, which are definitely greater than the experimental error. Further discussion of this nonlinearity will be postponed until after the evidence for mechanistic complexities has been discussed.

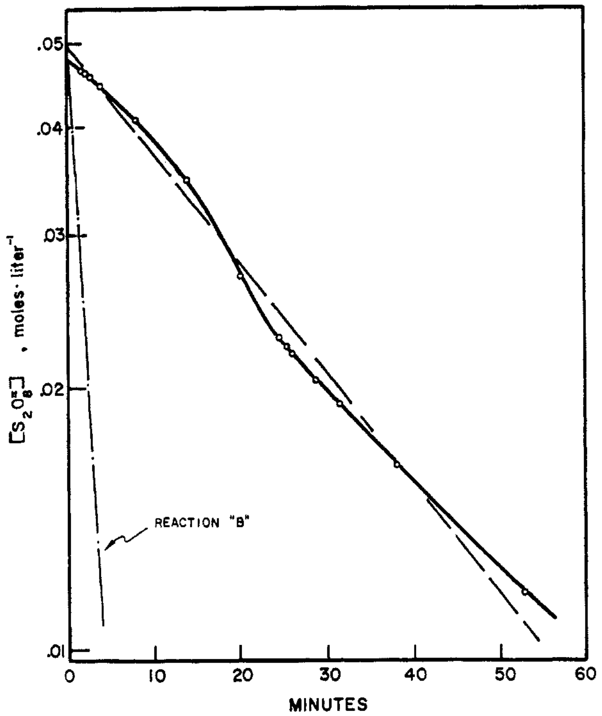

Fig. 4. Titration data demonstrating the sigmoid character of the first order plot for reaction A

Trace metal catalysis. The effect of EDTA on the rate is considered to be due to sequestration of trace metal impurities which exert a catalytic influence. Although it was observed that persulfate reacts slowly with higher concentrations of EDTA, probably by oxidation at nitrogen,[8] the inhibiting effect observed here with traces of EDTA is attributed to sequestration of trace metal catalysts rather than reaction with EDTA, as traces of substances with similar functional groups, but no strong chelating ability, gave no retardation of rate (see Table III).

In an attempt to discover the ion or ions responsible for the trace metal catalysis, a series of trace impurities were intentionally introduced into reacting solutions, and their effect on the rate of reaction A observed. From the series of ions—Ag^+, Ce^{+4}, Co^{+2}, Cr^{+3}, Cu^{+2}, Fe^{+2}, Fe^{+3}, Hg^{+2}, Mg^{+2}, Mn^{+2}, Ni^{+2}, Sn^{+4}, and Zn^{+2}—added so that their concentrations were approximately 10^{-5} M, only Cu^{+2} was observed to exert a noticeable catalytic effect. While this does not prove that Cu^{+2} is the only catalyst involved, it is certainly the most effective one observed. The presence of catalytic impurities was confirmed upon purification of the potassium peroxydisulfate by several recrystallizations from conductivity water. This reduced the initial rate of reaction A to a value approaching that observed in the presence of EDTA. Using recrystallized potassium peroxydisulfate, the initial rate of reaction A was then measured as a function of added Cu^{+2} ion. The data are summarized in Table IV. Assuming that Cu^{+2} is the impurity which is removed by the recrystallizations, the data allow estimates of the amount of Cu^{+2} originally present. Solutions of the unrecrystallized persulfate correspond to an added copper concentration of $10^{-5}M$. One recrystallization from conductivity water reduced the rate to that observed in the presence of 10^{-7} M Cu^{+2}, while two recrystallizations reduced the rate almost to that observed in the presence of EDTA.

TABLE IV

THE EFFECT OF RECRYSTALLIZED PERSULFATE AND ADDED CUPRIC ION ON THE INITIAL RATE OF REACTION A

$K_2S_2O_8$ Recrystallizations	Substance Added	Concentration Moles-l.$^{-1}$	Ratio Rate/ Minimum Rate[a]
0	None	—	7.9
1	None	—	4.6
2	None	—	1.5
3	None	—	1.9
1	EDTA	10^{-5}	1.0
2	Cu^{+2}	10^{-8}	2.5
2	Cu^{+2}	10^{-7}	4.5
2	Cu^{+2}	10^{-6}	7.3
2	Cu^{+2}	10^{-5}	7.9
2	Cu^{+2}	10^{-4}	8.6
2	Cu^{+2}	10^{-4}	8.6

$[S_2O_8^{--}]_0 = 0.049M$; $[R_2CHOH]_0 = 0.39M$; temperature $= 60.0°$; unbuffered solution

[a] The minimum rate, observed with EDTA present, had an average value of 0.45×10^{-3} moles/l.$^{-1}$/min.$^{-1}$

From the stability constant of the EDTA-Cu^{+2} complex[10] $\log K = 18.8$, negligible free Cu^{+2} obviously is present in solution with added EDTA. Copper is a reasonable impurity to expect in persulfate, whose solutions are known to dissolve metallic copper.[11] The heavy metal analysis of potassium peroxydisulfate reported on the reagent bottle, if attributed entirely to copper, is of the right order of magnitude to account for the observed impurities. Other cases of trace copper catalysis in persulfate reactions are known.[12-15]

The data in Table IV show that the dependence on added Cu^{+2} is not a simple order. Although an added Cu^{+2} concentration of 10^{-7} M more than quadruples the rate observed in its absence, further increasing the Cu^{+2} concentration by a factor of one thousand increases the rate by a factor less

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(10) R. W. Schmid and C. N. Reilley, *J. Am. Chem. Soc.*, **78**, 5513 (1956).

(11) G. C. Bond, B. M. Hill, and R. Tennison, *J. Chem. Soc.*, 33 (1959).

(12) T. L. Allen, *J. Am. Chem. Soc.*, **73**, 3589 (1951).

(13) C. H. Sorum and J. O. Edwards, *J. Am. Chem. Soc.*, **74**, 1204 (1952).

(14) O. A. Chaltykyan, A. N. Mamyan, and R. V. Mousesyan, *Nauch. Trudy Erevan. Gosudarst, Univ. Ser. Khim. Nauk*, **60**, 135 (1957); *Chem. Abstr.*, **53**, 10925 (1959).

(15) Y. K. Gupta and S. Ghosh, *J. Inorg. & Nuclear Chem.*, **11**, 62 (1959).

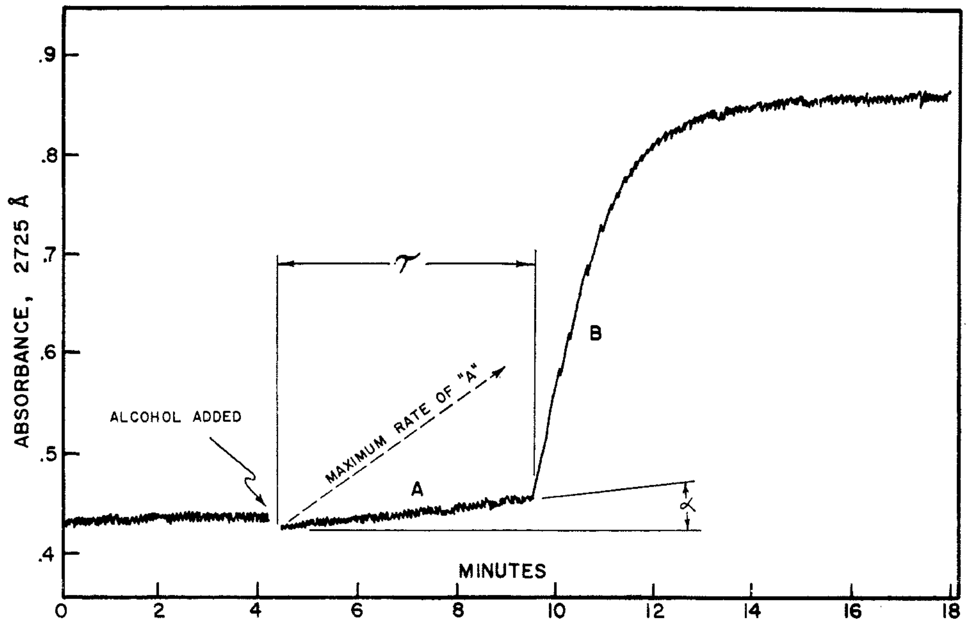

Fig. 5. A typical spectrophotometer trace at 2725 Å showing reaction A, reaction B, the induction period τ, and the initial angle α

than two. This indicates that the catalytic effect of Cu^{+2} reaches an upper limiting value at approximately 10^{-4} M. Reaction A must be zero order in copper ion above this concentration. This can account for the fact that previous workers have reported comparable rate constants, as at a Cu^{+2} concentration as low as 10^{-6} to 10^{-5} M, the rate is insensitive to small changes in copper concentration, although the small amount present has a very significant catalytic effect.

The length and rate of reaction A. A typical spectrophotometer trace is shown in Fig. 5 for a run at 60.0° in unbuffered solution using thrice recrystallized persulfate. Air is initially present, and the initial concentrations of persulfate and 2-propanol are 0.049M and 0.39M, respectively. The maximum rate of reaction A, observed in the presence of added Cu^{+2}, is indicated by the dashed line. There are two important variables which were measurable for reaction A as it was normally observed on the spectrophotometer trace. The first is the length of time elapsed between the addition of alcohol and the sudden increase in rate at the onset of reaction B. This corresponds to the length of time required to use up the dissolved oxygen. This time will be referred to as the length of the inhibition period, and identified by the symbol τ. There was negligible air space above the solution in the stoppered spectrophotometer cells, and for short τ the rate of diffusion of additional oxygen, as it dissolved, may be ignored. Hence, for a given set of conditions, τ is a measure of the original concentration of dissolved oxygen. Conversely, for a given original concentration of dissolved oxygen, τ is inversely proportional to the rate at which oxygen is consumed. The second variable is the tangent of the angle α produced by the recorder trace with the horizontal. For measurements made at identical initial persulfate concentration, this value is proportional to the initial rate of reaction A. The factors affecting these two variables were studied.

Let us first consider τ. Table III shows that it is essentially independent of added EDTA. It increased slightly in the presence of the maximum effective concentration of Cu^{+2}. It was inversely related to the initial alcohol concentration as shown in Fig. 6. This effect reached a limiting value at high alcohol concentration. As might be expected, it was strongly dependent on temperature, as this affected not only the rate of loss of oxygen, but also the solubility of oxygen. The observed data are presented in Table V. It was also observed that τ was as much as twice as long in buffered solution as in unbuffered; the reason for this is not completely clear.

TABLE V

THE TEMPERATURE DEPENDENCE OF REACTION RATES[a]

Temperature	τ, min.	Tangent α[b]	$k_{3/2}$(B)[c]
40°	124	0.044	—
45°	32	0.070	0.30
50°	19.3	0.105	0.46
55°	8.6	0.194	0.76
60°	6.4	0.270	1.45
65°	3.2	0.374	2.14
70°	2.6	0.499	2.85

[a] $[S_2O_8^{--}]_0$ = 0.049M; $[R_2CHOH]_0$ = 0.39M; unbuffered solution initially in equilibrium with air at 25°. [b] Proportional to the initial rate of reaction A. [c] Reaction B, units are $l.^{1/2}/mole^{1/2}/min.^{-1}$.

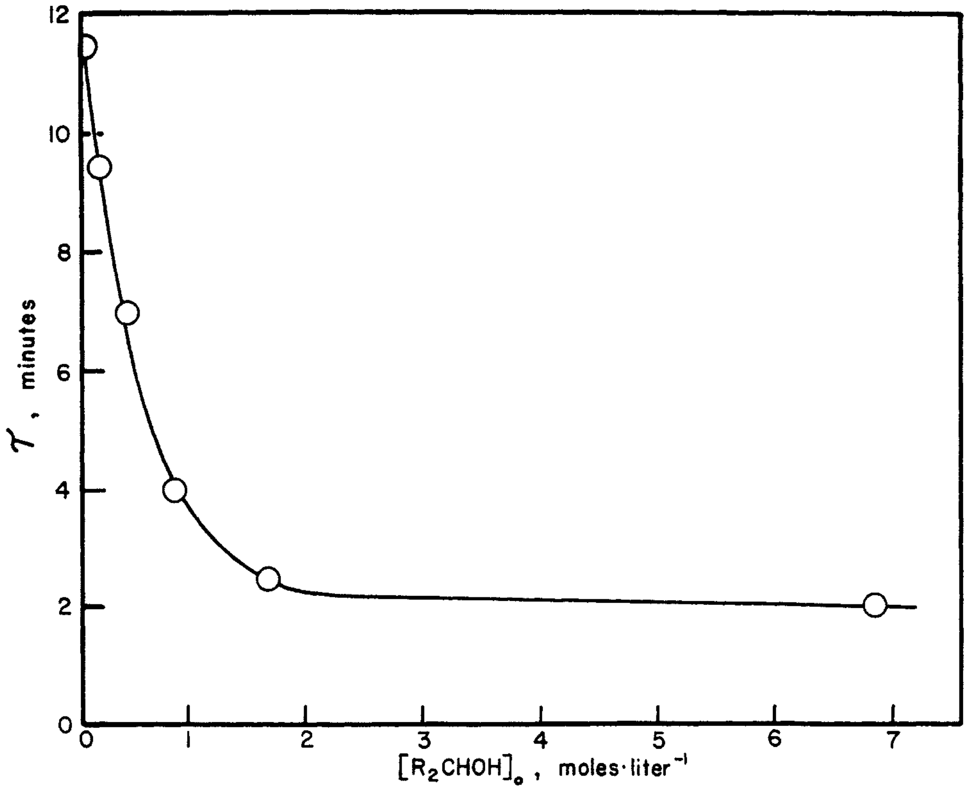

Fig. 6. Effect of alcohol concentration on the length of the induction period at 60°

TABLE VI

THE EFFECT OF ALCOHOL CONCENTRATION ON INITIAL RATES[a]

$[R_2CHOH]_0$, moles/l.$^{-1}$	Tangent α[b]	$k_{3/2}(B)$[c]
0.04	0.19	—
0.16	0.20	0.85
0.40	0.16	0.92
0.79	0.23	0.82
1.6	0.33	0.86
6.7	0.27	
	Avg. 0.23 ± 0.05	

[a] All measurements are at 60° and constant initial persulfate concentration (twice recrystallized). [b] Proportional to the initial rate of reaction A. [c] Rate constants units are l.$^{1/2}$/mole $^{-1/2}$/min.$^{-1}$

The second variable, the initial rate of reaction A, was strongly dependent on the presence of EDTA or traces of Cu^{+2} as has already been discussed. The initial rate was independent of oxygen concentration. This may be seen in Figs. 2 and 3, as the initial rates are identical for different initial concentrations of dissolved oxygen. The sharp discontinuity in the spectrophotometer traces upon the exhaustion of dissolved oxygen provides additional evidence that the rate is independent of dissolved oxygen concentration until it is completely used up.

The initial rate was also independent of alcohol concentration, above 0.04*M*, as demonstrated by the data of Table VI. This zero order behavior is consistent with the data of Tables I and II and with the findings of previous workers[4,5] under conditions where oxygen was not excluded. Although there is scatter in the measured initial rate values, there is clearly no rate dependence of the type of a kinetic order on alcohol concentration. Furthermore, this result predicts that the rate of reaction A should be independent of the nature of the alcohol; this was found in the experiments presented in Fig. 1.

The temperature dependence of the initial rate of A is included in Table V. It corresponds to an apparent activation energy of 18 kcal./mole. As $1/\tau$ is proportional to the rate at which dissolved oxygen is consumed, an approximate value for the activation energy of the reaction by which oxygen is lost may also be calculated. Although the solubility of dissolved oxygen varies with temperature, there was probably insufficient time for equilibrium solubility to be reached. The calculation was therefore made assuming identical initial oxygen concentration, regardless of temperature. A value of 25 to 27 kcal./mole was obtained from the resulting, approximately linear Arrhenius plot.

From the evidence which has just been presented, it may be seen that these two variables, τ and tangent α, which are related to the oxygen inhibition and the Cu^{+2} catalysis, respectively, are in some ways independent. The reaction with dissolved oxygen, which blocks the rapid reaction B, is not affected by the presence or absence of Cu^{+2} catalysis. The presence of oxygen, however, seems

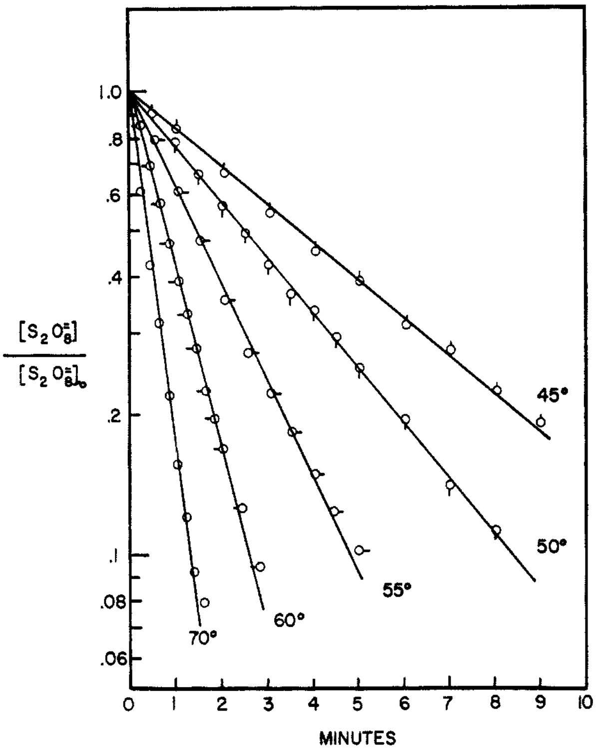

Fig. 7. Pseudo-first-order rate plots for reaction B at several temperatures; $[S_2O_8^{--}] = 0.049M$ and $[R_2CHOH] = 0.39M$

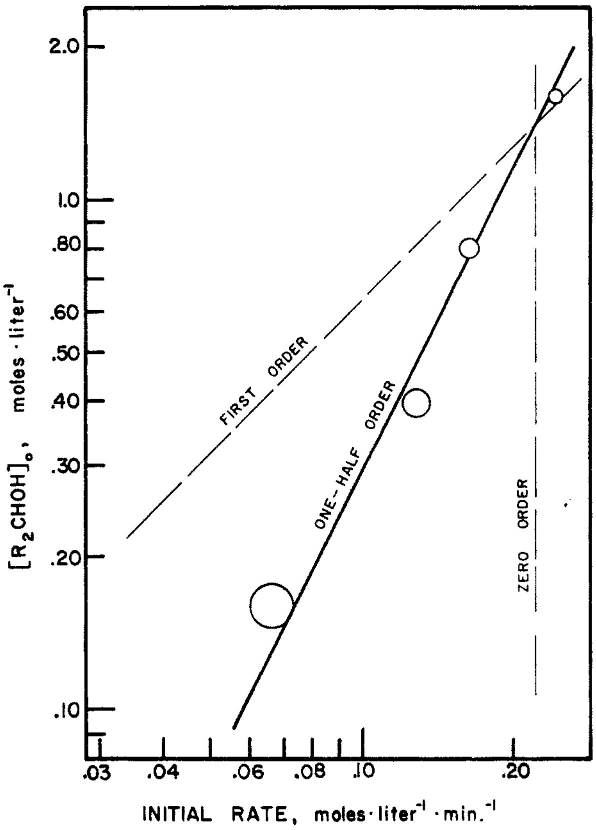

Fig. 8. Order plot demonstrating the dependence of the rate of reaction B on alcohol concentration

to be necessary for the metal catalysis, as reaction B is unaffected by Cu^{+2} or EDTA. There must be two reaction paths in reaction A. When the metal catalyzed path is removed by EDTA, the residual reaction—call it A_0—is simply the reaction by which dissolved oxygen is lost. Since the presence of Cu^{+2} catalysis does not shorten τ, the catalysis must proceed by a mechanism which does not introduce intermediates capable of increasing the rate of consumption of oxygen. This places rather stringent restrictions on the type of mechanisms which can be considered for reactions A and A_0. Unfortunately, neither EDTA nor recrystallization completely removed the influence of metal ions on the value of α, for this angle never decreased to the value predicted from the intrinsic rate of decomposition of persulfate. Therefore, in order to draw conclusions about reaction A_0, we limited ourselves to the information obtained from τ values.

Reaction B kinetics. Reaction B takes place only in the absence of oxygen. The introduction of a minute amount of oxygen into the reaction cell after B began immediately stopped B and the slower reaction A began again. As earlier workers apparently did not exclude oxygen, the kinetics of this reaction between persulfate and 2-propanol have not previously been studied.

Addition of EDTA or recrystallization of persulfate had no significant effect on the rate of reaction B as may be noted from the data of Table III. In experiments designed to test the influence of Cu^{+2} on the rate of reaction B, three runs with 0, 10^{-5}, and 10^{-4} M Cu^{+2} added were carried out with twice-recrystallized persulfate and de-ionized water. The rate constants obtained were 1.08, 1.07, and 1.06 $l.^{1/2}/mole^{-1/2}/min.^{-1}$, the variation observed therein is less than the expected error (see below).

The reaction appears pseudo-first-order in persulfate over four or five half lives when run in the presence of a large excess of alcohol. Pseudo-first-order rate plots for reaction B are shown in Fig. 7. The excellent linearity of the lines over 90% of the reaction confirms the order in persulfate. The observed rate constants are a function of the initial alcohol concentrations, however. By varying the initial alcohol concentration over a ten-fold range at constant initial persulfate concentration, the order in alcohol was shown to be one-half; some data are presented in Table VI. This one-half order behavior is demonstrated graphically in Fig. 8. The rate law for reaction B is therefore

$$\frac{d[S_2O_8^{--}]}{dt} = k[S_2O_8^{--}][R_2CHOH]^{1/2}$$

The apparent activation energy of reaction B was determined from runs at 45°, 50°, 60°, 65°, and 70° with the data presented in Table V. Within the experimental error, a linear Arrhenius plot was obtained, with a slope corresponding to an activation energy of 21 kcal./mole.

After our first trials dealing with the effect of gases on rate, a procedure designed to minimize the diffusion of oxygen into the cell was worked out. Using this procedure, twenty-eight experiments at 60° giving values (from initial slopes) of the three-halves order rate constants were carried out. Values for initial rate constants between 0.70 and 1.08 l.$^{1/2}$/mole$^{-1/2}$/min.$^{-1}$ were obtained for twenty-six experiments; the other two were somewhat low (0.50 and 0.52), which suggests that oxygen was not completely excluded in these cases. The average constant and the average deviation for the twenty-six experiments was 0.91 ± 0.09 in units of l.$^{1/2}$/mole$^{-1/2}$/min.$^{-1}$ Although these rate constants from initial slopes of the B-part are not quite as accurate as those of Fig. 7 and 8, they show that the variation in $k_{3/2}$ is encouragingly small for such a complicated system; also, the inhibition period τ was never completely eliminated. However, the observed value of $k_{3/2}$ did not depend on the length of the inhibition period.

Comparison of reaction rates. Before proceeding to a discussion of possible mechanisms for these reactions, it will be helpful to make a summary comparison of the relative rates of all the reactions involved. This is given in Table VII below. The rates are based on the thermal decomposition of persulfate as unity. To make them consistent, they refer to initial rates which have been corrected to standard conditions of temperature and reactant concentrations. Due to changes in buffer, pH, trace impurities, etc. from one observer to another, the rate ratios may be expected to be only approximate. The fact that previous work lay in the range of the oxygen-inhibited, copper-catalyzed reaction is unmistakable, however.

TABLE VII

COMPARISON OF RELATIVE RATES[a]

Reactant	In Presence of	Observer		Relative Rate
H_2O	Air	Kolthoff[7]		1.000
H_2O	Air	Wiberg	5	0.8
H_2O	Air	[b]	1b	1.1
R_2CHOH	Allyl acetate	Wiberg[5]		0.8
R_2CHOH	Air, EDTA	[b]	1a	5
R_2CHOH	Air, EDTA	[b]	1b	27
R_2CHOH	Air,[c]	[b]	1b	40
R_2CHOH	Air	[b]	1a	22–44
R_2CHOH	Air	Wiberg	5	46
R_2CHOH	Air	Levitt	4	65
R_2CHOH	Air; $10^{-4}M$ Cu^{+2}	[b]	1b	235
R_2CHOH	Nitrogen	[b]	1b	1800
R_2CHOH	Nitrogen, EDTA	[b]	1b	1800
R_2CHOH	Nitrogen; $10^{-4}M$ Cu^{+2}	[b]	1b	1800

[a] Based on initial conditions; $[S_2O_8^{--}]_0 = 0.049M$; $[R_2CHOH] = 0.39M$; 60°. [b] This study. [c] With twice recrystallized $K_2S_2O_8$.

DISCUSSION

Points of contention. Before the actual mechanistic steps for this oxidation reaction can be discussed, certain points of disagreement in the literature must be resolved. It is the purpose of this section to go over the evidence in order to arrive at a satisfactory conclusion on each point.

In this study, two previously unreported kinetic factors have been uncovered. The first of these is the catalysis up to a limiting rate of the persulfate-alcohol reaction by traces of copper ion. The evidence for this catalysis may be summarized as follows: a) Small amounts of Na_2H_2Y markedly slowed down the rates (in the A part) whereas comparable amounts of weakly coordinating reagents such as glycine or triethylamine had no effect on the rate, b) two recrystallizations of the potassium persulfate from conductivity water resulted in a decrease in rate approaching that observed in the presence of Na_2H_2Y, and c) addition of small amounts of copper ion caused a large increase in the rate when recrystallized persulfate was used.

The other factor, oxygen inhibition, is demonstrated by the following pieces of evidence: a) the sudden change in rate at the end of the A part is evidence for depletion of an inhibitor, b) the length of time of the A part (τ) varied directly with the initial oxygen concentration, c) shaking air into the cell after the B part has started causes the B part to cease and a new part A to begin, and d) the oxygen inhibition mechanism postulated below predicts a length of time for part A that agrees satisfactorily with the observed length.

It seems certain that the oxidation of alcohols by peroxydisulfate ion is a free radical reaction. In view of the fact that a polar mechanism has been put forth,[4,6] the evidence for the radical mechanism is worth reiterating: a) The rate of reaction is a sensitive function of the experimental conditions, b) the reaction is inhibited by oxygen which is normal for a chain reaction involving an organic radical, c) peroxydisulfate ion is known[7,9] to decompose by a radical mechanism, d) allyl acetate lowers the rate of loss of peroxydisulfate in the presence of alcohol to that observed for its free radical decomposition[5] thus no path independent of sulfate ion radicals can be present, e) Cu^{++} ion influences the rate of part A reaction, f) a one-half order as in the 2-propanol concentration dependence of the part B reaction is a characteristic of a radical reaction, and g) changes in order as concentrations vary[4] are found where several termination steps can compete.

One question which has been raised heretofore now seems answered: There seems to be no significant interaction of alcohol and peroxydisulfate in the initiation step. The reasons behind this conclusion are as follows: a) The overall order of the part B reaction is three-halves whereas it would have to be two if a bimolecular reaction constituted the initiation step, b) the rates of part A reactions are insensitive to alcohol concentration and to alcohol nature, c) the rate of loss of persulfate in the presence of alcohol and allyl acetate agrees with the known decomposition rate for peroxydisulfate ion alone,[5] and d) no evidence for a bimolecular initiation step was found in the studies of Kolthoff, Meehan, and Carr[3] or of Bawn and Margerison.[16]

The present study and that of Wiberg[5] have brought forth considerable evidence which is contrary to the ionic mechanism postulated by Levitt for the peroxydisulfate oxidation of 2-propanol.[4,6] Some experimental points bearing on this matter are worth mentioning. a) There is no dependence of rate on sulfate ion concentration which would bear out the inverse first order dependence required by his mechanism. b) There has not been any evidence for a thermal peroxydisulfate–sulfate sulfur exchange[5,9,17] as required by his mechanism. c) The experimental observations of rate inhibition by allyl acetate[5] and by oxygen are positive proof that the rate constants found by Levitt must have arisen from a free-radical initiated mechanism. Any polar mechanism would be unaffected by these additives. d) Similarly the copper ion catalysis and the $\mathrm{Na_2H_2Y}$ inhibition are evidence against a polar displacement mechanism of oxidation. In view of the evidence, the mechanisms of Levitt[4,6] for the persulfate oxidation of 2-propanol must be considered incorrect. Indeed, the general applicability of any mechanism directly or indirectly involving a reversible, heterolytic reaction of persulfate such as proposed by Levitt for the oxidation of other substrates[6] also must be seriously questioned.

While we reject the mechanistic proposals of Levitt, we feel it is important to point out that the experimental data are not being questioned. Levitt and Malinowski[4] report and our results confirm that the reaction is zero order in alcohol concentration (when oxygen is present, of course). Also some of the kinetic plots of their latest paper seem to show the same soft sigmoid character that we have observed. Finally, the values for the first order rate constants which they reported are in the range of those rates we have observed for the A part of the reaction. For example we obtained initial rate values of 4.85×10^{-4} and 13.3×10^{-4} mole/l.$^{-1}$/min.$^{-1}$ for runs with no added copper and with 5×10^{-5} *M* cupric ion respectively, under a set of conditions (60°, $[\mathrm{S_2O_8}^{--}] = 0.0485M$, $[\mathrm{R_2CHOH}] = 0.396M$) for which the data of Levitt and Malinowski predict an initial rate value of 9.05×10^{-4}. Evidently, they never exhausted the oxygen supply nor did they remove the trace amounts of copper present in their reagents, and thus always observed the A portion of the reaction.

Mechanistic patterns. The results obtained here are surprisingly cleancut in that there are few kinetic patterns which can fit all of the data. Starting with reaction B which seems to be the least complicated part, the postulated chain mechanisms is

$$\mathrm{S_2O_8}^{--} \xrightarrow{k_1} 2\mathrm{SO_4}^{\underset{\cdot}{-}}$$

$$\mathrm{SO_4}^{\underset{\cdot}{-}} + \mathrm{R_2CHOH} \xrightarrow{k_2} \mathrm{HSO_4}^{-} + \mathrm{R_2\dot{C}OH}$$

$$\mathrm{R_2\dot{C}OH} + \mathrm{S_2O_8}^{--} \xrightarrow{k_3} \mathrm{R_2CO} + \mathrm{HSO_4}^{-} + \mathrm{SO_4}^{\underset{\cdot}{-}}$$

$$\mathrm{R_2\dot{C}OH} + \mathrm{SO_4}^{\underset{\cdot}{-}} \xrightarrow{k_4} \mathrm{R_2CO} + \mathrm{HSO_4}^{-}$$

This predicts the rate law

$$\mathrm{R} = \left(\frac{k_1k_2k_3}{k_4}\right)^{1/2} [\mathrm{S_2O_8}^{--}][\mathrm{R_2CHOH}]^{1/2}$$

in agreement with the observed expression. Since we have found that the chain length is greater than one thousand (see Table VII), the activation energies for k_2, k_3, and k_4 should be small; one predicts that the overall activation energy for the chain should lie between $^1/_2\mathrm{E}_1$ and E_1 where E_1 is the activation energy of the k_1 step and has a value of about 31 kcal./mole^{-1}.[7,16] Our observed activation energy is 21 kcal./mole^{-1}, which is in good accord. Also, the rate constant observed for the B part should depend on the nature of the alcohol, as the ease of carbon-hydrogen bond breaking in the k_2 step would be expected to increase with methyl substitution on the carbinol carbon. Here again the agreement is excellent, for the rate of loss of persulfate in the B part is a factor of forty lower when methanol is oxidized than when 2-propanol is oxidized.[1b]

Rate inhibition by allyl acetate[5] and by oxygen must involve trapping of the radicals which carry the chain in the mechanism of part B. As persulfate has been reported to initiate polymerization of vinyl compounds through the sulfate ion radical,[18] it seems reasonable that allyl acetate reacts with the sulfate ion radical. Inhibition by oxygen, on the other hand, must involve the reducing radical $\mathrm{R_2\dot{C}OH}$.

For the data of part A for the case of no contribution from metal ion catalysis, we postulate the following steps:

$$\mathrm{O_2} + \mathrm{R_2\dot{C}OH} \xrightarrow{k_5} \cdot\mathrm{OOR_2COH}$$

$$\cdot\mathrm{OOR_2COH} + \mathrm{R_2CHOH} \xrightarrow{k_6} \mathrm{HOOR_2COH} + \mathrm{R_2\dot{C}OH}$$

$$2\cdot\mathrm{OOR_2COH} \xrightarrow{k_7} \mathrm{O_2} + \mathrm{HOOR_2COH} + \mathrm{R_2CO}$$

The inhibition by oxygen can be traced to a very high rate constant for k_5 coupled with a low k_6 reactivity so that the peroxidic radicals build up in sufficient concentration to terminate the chain in the k_7 step. Such steps and their reactivities are

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(16) C. E. H. Bawn and D. Margerison, *Trans. Faraday Soc.*, **51**, 925 (1955).

(17) (a) P. C. Riesbos and A. H. W. Aten, Jr., *J. Am. Chem. Soc.*, **74**, 2440 (1952). (b) H. Elkeles and C. Brosset *Svensk. kem. Tidski.*, **65**, 26 (1953). (c) R. L. Eager and K. J. McCallum, *Can. J. Chem.*, **32**, 692 (1954).

(18) P. Bartlett and K. Nozaki, *J. Polymer Sci.*, **3**, 216 (1948).

discussed in the recent review on fundamental processes of autoxidation by Russell.[19]

Application of steady state treatment to the sequence k_1, k_2, k_5, k_6, and k_7 leads to the rate law

$$\frac{-d[O_2]}{dt} = k_1[S_2O_8^{--}] + k_6\left(\frac{k_1}{k_7}\right)^{1/2}[S_2O_8^{--}][R_2CHOH]$$

for the take-up of dissolved oxygen. As the inhibition period τ is related to the reciprocal of the rate, this law predicts that the value of τ should be related to the amount of oxygen initially present but not dependent on oxygen concentration as a kinetic order. The dependence on alcohol concentration also is as expected, for τ does decrease as alcohol concentration increases.

Using the step k_1 and the oxygen solubility in water for both of which we have values from the literature, one can compute an inhibition time using the mechanistic sequence, k_1, k_2, k_5, and k_7. For one experiment with an observed τ value of seventeen minutes, the calculated value was sixty minutes; considering that k_6 which would lower the τ value was not taken into account, the agreement is good.

It is worth noting here that step k_6 demands a dependence of slope α for reaction A_0 on both concentration and nature of alcohol. This was not observed as we were never able to eliminate completely the metal ion catalysis rate which swamps out A_0 because of its greater magnitude.

It would indeed be difficult to postulate a mechanism for the metal-catalyzed portion of the reaction but for the fact that the experimental data narrow down the number of possibilities. Criteria which must be satisfied in any mechanism postulated for the metal-catalyzed case include the following: a) The rate becomes independent of copper ion concentration above 10^{-4} M, b) the rate is independent of alcohol concentration or nature above 0.05 M, c) the inhibition time is not shortened (τ increases somewhat as copper concentration increases), d) some reactive species (from oxygen interaction?) other than those of the part B reaction must initiate the metal-catalyzed reaction as the part B rate is not affected by added copper or by added Na_2H_2Y, and e) no new free radicals can be formed.

We postulate the following steps:

$$H^+ + \cdot OOR_2COH + Cu^{+2} \xrightarrow{k_8} Cu^{+3} + HOOR_2COH$$

$$Cu^{+3} + R_2CHOH \xrightarrow{k_9} Cu^+ + R_2CO + 2H^+$$

$$Cu^+ + S_2O_8^{--} \xrightarrow{k_{10}} Cu^{+3} + 2SO_4^{--}$$

$$2Cu^+ \xrightarrow{k_{11}} Cu_0 + Cu^{+2}$$

$$Cu_0 + S_2O_8^{--} \xrightarrow{\text{fast}} Cu^{+2} + 2SO_4^{--}$$

In this sequence, step k_8 provides an entry into a cyclic redox chain involving Cu^+ and Cu^{+3}. Steps k_9 and k_{10} constitute the nonradical propagation steps which carry the main oxidation of alcohol in reaction A. Step k_{11}, which is the disproportionation of cuprous ion, acts as a chain termination step. The step k_{12} is postulated as a means of returning Cu^0 to Cu^{+2} without the formation of radicals.

The disproportionation reaction of cuprous ion (step k_{11}) is well known in aqueous solution.[20] The oxidation of zero valent copper to cupric ion (step k_{13}) is also known.[11] Knowledge of the tripositive oxidation state of copper is admittedly limited; the evidence has been summarized by Sneed, Maynard and Brasted[21] and Latimer[22] has given approximate oxidation potentials. Of particular pertinence to the presence study is the fact that a series of complex salts containing tripositive copper have been prepared by persulfate oxidation.[23] If these steps are combined with others already considered, the following rate law for the case of maximum copper-catalysis rate is derived:

$$R = \left(\frac{k_1}{k_{11}}\right)^{1/2} k_{10}[S_2O_8^{--}]^{3/2}$$

This rate law predicts a rate which is independent of alcohol and of metal in agreement with the experimental results. Further it suggests an explanation for the sigmoidal shape of the first order plots of part A. Often in reactions where intermediates are present, a finite time is required to reach the steady state concentration. Thus, the initial portion of the reaction indicates an autocatalysis. Toward the other end, however, the first order rate constant should fall off if the true order is greater than one. This combination of an initial build-up in intermediate concentration and a final order of three-halves can therefore give a first order plot that has a sigmoid appearance.

One surprising aspect of the experimental restrictions is that practically no alternative steps can be postulated for this reaction without contradicting some piece of experimental information. Particularly, reactions of the type

$$S_2O_8^{--} + Cu^{++} \longrightarrow SO_4^{\cdot-} + SO_4^{--} + Cu^{+3}$$

which have been proposed to explain catalysis by other metal ions of persulfate oxidations[16] must be excluded in our case. They predict a first order dependence on metal ion concentration, as well as produce additional $SO_4^{\cdot-}$ radicals which would shorten τ.

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(19) G. A. Russell, *J. Chem. Ed.*, **36**, 111 (1959).

(20) T. Moeller, "Inorganic Chemistry," John Wiley and Sons, New York (1952); pg. 826.

(21) M. C. Sneed, J. L. Maynard, and R. C. Brasted, *Comprehensive Inorganic Chemistry*, Vol. II, D. Van Nostrand Co., Inc., New York (1954), pg. 111-113.

(22) W. M. Latimer, *Oxidation Potentials*, Prentice-Hall New York (1938), Chap. 11.

(23) L. Malatesta, *Gazz. chim. ital.*, **71**, 476, 580 (1941).

A possible alternative step for initiating the metal catalyzed chain is the reaction

$$HOOR_2COH + Cu^{+2} \xrightarrow{k_{8b}} Cu^+ + H^+ + \cdot OOR_2COH$$

which would replace k_8. While our data do not completely eliminate this as a possibility, it has the disadvantage that it would indicate a slight dependence of the metal-catalyzed rate on concentration and nature of alcohol (because of the k_6 step.) It is encouraging to note that all the types of steps and of intermediates are known types.

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PROVIDENCE, R. I.

[CONTRIBUTION FROM THE RESEARCH LABORATORY, VETERANS ADMINISTRATION CENTER, WICHITA, KANSAS, AND THE CHEMICAL LABORATORIES OF THE UNIVERSITY OF WICHITA]

The Reaction of Cholesteryl *p*-Toluenesulfonate with Dimethyl Sulfide and Methanethiol[1]

N. F. BLAU AND C. G. STUCKWISCH

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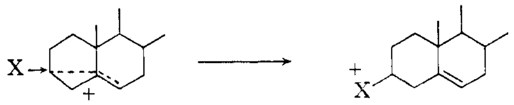
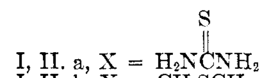
Dimethyl sulfide reacts with cholesteryl p-toluenesulfonate to give 3β-dimethylsulfonio-5-cholestene p-toluenesulfonate. Cholesteryl p-toluenesulfonate and methanethiol yield chiefly 3β-methylthio-5-cholestene together with small amounts of 3α-methylthio-5-cholestene and 3,5-cyclo-6-methylthiocholestene. Reasons for the structural and stereochemical assignments are given and some reactions of the compounds are described.

During recent years a number of investigations have been directed toward introducing sulfur-containing groups into natural steroids in order to study the effect of such substitution on physiological activity. Cholesterol has been converted to 5-cholestene-3β-thiol by reaction of cholesteryl p-toluenesulfonate with thiourea[2] or potassium thiocyanate[3,4] followed by hydrolysis. The conversion of steroidal ketones to thioketones has been accomplished recently[5,6] and alkanethiolic acids and mercaptans have been added to appropriately unsaturated steroidal ketones.[7,8]

Our interest in sulfur-containing steroids stems from a broad investigation being carried out in these laboratories into the chemical[9] and physiological properties of sulfur compounds, the sulfonium compounds in particular. Dodson and Riegel[10] have shown that the reaction product of thiourea with cholesteryl p-toluenesulfonate[2] is a 3β-thiouronium derivative. The reaction is very probably a nucleophilic attack by thiourea on a hybrid carbonium ion as depicted in formulas Ia→IIa.



I II



$$\text{I, II. a, X} = H_2N\overset{\overset{\large S}{\|}}{C}NH_2$$
$$\text{I, II. b, X} = CH_3SCH_3$$

The 3β-configuration (equatorial) for the introduced isothiouronium group is in accord with current views on the stereochemistry of reactions[11] involving nucleophilic displacements in homoallylic systems of the type found in 5-cholestenes.

Thus it seemed to us, that mechanistically it was possible to achieve a direct synthesis of 3β-dialkylsulfonio-5-cholestenes by the reaction of dialkyl sulfides with cholesteryl p-toluenesulfonate (Ib→IIb). Indeed, this proved to be the case. In nitromethane as a solvent, dimethyl sulfide reacted with cholesteryl p-toluenesulfonate to yield 3β-dimethylsulfonio-5-cholestene p-toluenesulfonate (IIb) in 90% yield.

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