Kinetics and Mechanisms of the Spontaneous and Metal-Modified Oxidations of Ethanol by Peroxydisulfate Ion[1a,b]

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The oxidation of ethanol by peroxydisulfate has been found to proceed by three distinct paths, the first in the presence of O_2 (path A), the second in the absence of oxygen (path B), and the third in the presence of several metal ions, particularly Cu(II) (path C). The first two paths are similar to those observed for the 2-propanol and methanol oxidations; however, some differences are noted. Included are results showing inhibition by O_2, by allyl acetate, and by product acetaldehyde. After minimization of effects due to catalysts and inhibitors, the observed rate law for path B was found to be rate $= k[S_2O_8^{2-}]^{3/2}$. A survey of metal salts as potential catalysts has shown that copper and silver ions act as catalysts while ammonium molybdate apparently acts as an inhibitor. A detailed study of the effect of cupric ion on the oxidation showed that the stoichiometry (including secondary oxidation of aldehyde product) was not changed by the metal ion, but that the rate law became rate $= k_{3/2}'[S_2O_8^{2-}][Cu(II)]^{1/2}$. Radical chain mechanisms which are consistent with stoichiometry, rate laws, and other kinetic effects are presented.

As a part of our continuing study of the peroxydisulfate oxidation of alcohols, we decided to look at a primary alcohol, specifically ethanol, as reductant. This alcohol presents the possibility of finding a behavior intermediate between those of 2-propanol[2] and methanol.[3]

A number of investigations which bear on the ethanol oxidation have been carried out.[4-7] Prior to our study, however, there existed an inconsistency between the apparent rate law which suggested the bimolecular initiation step (eq 1) while the results from

$$CH_3CH_2OH + S_2O_8^{2-} \longrightarrow CH_3\dot{C}HOH + HSO_4^- + SO_4\cdot^- \quad (1)$$

the use of radical traps (allyl acetate[3b,4] and diphenylpicrylhydrazyl[5]) were consistent only with the unimolecular initiation step (eq 2). Further, since our

$$S_2O_8^{2-} \xrightarrow{k_{1a}} 2SO_4\cdot^- \quad (2)$$

previous studies[2,3] showed that oxygen inhibition, aldehyde inhibition, and copper ion catalysis must be considered in alcohol oxidations (but had not been in the ethanol case), a careful study of the oxidation of ethanol by peroxydisulfate was warranted; in the course of this study, we have made the first detailed study of metal ion catalysis in such reactions.

Experimental Section

Distilled 95% ethanol was used for both kinetic and stoichiometric determinations. The $K_2S_2O_8$ was Baker and Adamson reagent grade, recrystallized twice from demineralized water. The acetaldehyde and allyl acetate were Eastman Organic Chemicals, usually distilled just before use. The cupric sulfate, anhydrous powder, was Baker and Adamson reagent grade and was used with no further purification. The 2,2,2-trifluoroethanol was K & K, and the 2,3-butanediol was Matheson Coleman and Bell; both alcohols were distilled (Vigreux column) before use. All other chemicals were reagent grade and were used without further purification. The demineralized water was obtained from a Bantam demineralizing column of the Barnstead Still and Sterilizer Co.

For the most part, kinetic runs were carried out spectrophotometrically using techniques similar to those of the previous studies.[2,3a] As both acetaldehyde and peroxydisulfate absorb in the ultraviolet, only a limited choice of convenient wavelengths was available. Most of the data was taken in the range below 240 nm, where a significant change in absorption obtains during the course of a kinetic run. Details are reported elsewhere.[8] With allyl acetate present, it was necessary to use a titrimetric technique.[3b,8]

Depending on the wavelength chosen, it was possible to analyze spectrophotometrically for peroxydisulfate (below 240 nm) or for acetaldehyde (ϵ 12.0 at λ_{max} 280 nm and 70°). Knowledge of the concentration of aldehyde was particularly important because of the stoichiometric complications.

The stoichiometric experiments that were performed in order to determine the total acid produced as a function of the ethanol-to-peroxydisulfate ratio were carried out in 5- or 10-cc ampoules and the reaction solution was titrated at infinite time with 0.05 or 0.1 *M* sodium hydroxide to the thymol blue (basic range pH 8.0–9.6) end point.

The vpc detection data for the glycol (2,3-butanediol) were obtained on a flame ionization Aerograph 200 vpc using a 6 ft × 0.125 in. aluminum tubing using FFAP (10%) as the liquid phase and Chrom W as the solid support.

A Fortran program, similar to that of Wiberg,[9] was written[8] to facilitate the calculations of rate constants from spectrophotometric data.

Results

General.—A number of characteristics of the ethanol oxidation by peroxydisulfate are akin to those characteristics reported[2-4,6] for oxidations of other alcohols; these will be mentioned here without further substantiation. Oxygen gas is an inhibitor; the rate of oxidation while oxygen is present is barely above the rate due to spontaneous decomposition of peroxydisulfate. At the instant the last bit of oxygen is used up, a sudden end to the "induction period" (denoted part A) is observed, and the faster rate of part B commences. In Figure 1, the fashion by which oxygen gas influences the behavior of this oxidation reaction is clearly seen. Product aldehyde is known to be a mild inhibitor.[1b,3a] Allyl acetate, both in the presence and absence of copper ion, lowers the rate of loss of peroxydisulfate to the level of the spontaneous decomposition; allyl

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[1] (a) Abstracted from the Ph.D. thesis of A. R. Gallopo, Brown University, 1967. (b) A preliminary account of some of this work has been published: J. O. Edwards, A. R. Gallopo, and J. E. McIsaac, Jr., *J. Amer. Chem. Soc.*, **88**, 3891 (1966). (c) NASA Fellow, 1965–1966.

[2] D. L. Ball, M. M. Crutchfield, and J. O. Edwards, *J. Org. Chem.*, **25**, 1599 (1960); see also references therein.

[3] (a) J. E. McIsaac, Jr., and J. O. Edwards, *ibid.*, **34**, 2565 (1969); (b) P. D. Bartlett and J. D. Cotman, *J. Amer. Chem. Soc.*, **71**, 1419 (1949).

[4] I. M. Kolthoff, E. J. Meehan, and E. M. Carr, *ibid.*, **75**, 1439 (1953).

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

[6] M. Santappa and L. R. Subbaraman, *Curr. Sci.*, **33**, 208 (1964).

[7] (a) L. R. Subbaraman and M. Santappa, *Proc. Indian Acad. Sci.*, **64**, 345 (1966); (b) *Z. Physik. Chem.*, **48**, 163 (1966).

[8] Ph.D. thesis of A. R. G.; see ref 1a. Procedures, results, and discussion in considerable detail can be found therein.

[9] K. B. Wiberg, "Physical Organic Chemistry," Wiley, New York, N. Y., 1964, p 560.

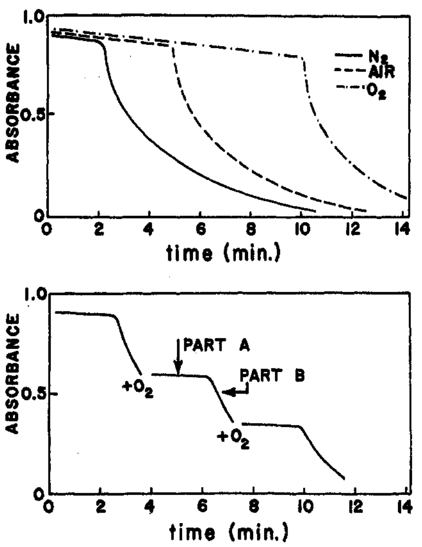

Figure 1.—The relative length of the induction period (part A) as a function of oxygen concentration (as established by nature of gas bubbled through solution before start of reaction) and a spectrophotometric plot showing how part B of reaction can be changed back to part A on reintroduction of oxygen.

alcohol also lowers the rate, but it is not quite so effective as allyl acetate. As expected, copper(II) under certain conditions is a catalyst for the reaction.

Under some conditions (carefully purified reactants and water, etc.), the rate of reaction during the induction period gave a rate constant value of 1.4×10^{-5} min^{-1} at 70°,[10] which is the constant reported for loss of peroxydisulfate in pure water. This indicates that the rate of radical formation is the same when alcohol is present as when alcohol is absent.

A search using glc for 2,3-butanediol as a possible product of the ethanol oxidation gave conclusive results. The standards used in the analysis showed that the amount of glycol formed even by chain termination alone would be readily detectable (approximately ten times background). We found none; thus the predominant (90%) termination product must also be aldehyde. No ethyl acetate was detected in either glc or the stoichiometric studies.

It is appropriate to discuss this oxidation reaction in three sections. The initial period during which the reaction is inhibited by dissolved oxygen is designated part A and the reaction is said to proceed by path A. The reaction after initiation of the faster section is termed part B, and is subdivided on the basis of copper additive. The mechanism in the absence of copper(II) is termed path B, and the mechanism when copper is present is termed path C.

Stoichiometry.—Because of the complications during the initial period (see below), a careful study of the stoichiometry was not feasible. On the other hand, the stoichiometry during the second part for both paths B and C was carefully investigated, and these data supply an important clue as to mechanism.

The predominant stoichiometry of the reaction in the absence of oxygen, with and without the presence of copper(II), was confirmed to be

$$S_2O_8^{2-} + CH_3CH_2OH \longrightarrow CH_3CHO + 2HSO_4^- \qquad (3)$$

This was based on yields of acetaldehyde, on titration of the total acid produced, and on the unchanging absorbance at an isoabsorptive point (270 nm at 70°) for the production of acetaldehyde and the disappearance of peroxydisulfate.

The yields of acetaldehyde and initial rates of reaction as a function of the ethanol-to-peroxydisulfate ratio are listed in Table I. The yields of acetaldehyde are essentially constant at 100 ± 1% when the ethanol-to-peroxydisulfate ratio is 40 or above, and the yields are seen to decrease when this ratio falls below about 40. This indicates that the mole ratio of acetaldehyde produced to peroxydisulfate reacted is 1:1 when the ethanol-to-peroxydisulfate ratio is 40 or above.

TABLE I

INITIAL RATES AND PER CENT YIELD OF ALDEHYDE AS A FUNCTION OF ETHANOL-TO-PEROXYDISULFATE RATIO AT 70°[a]

$[EtOH]_0$, M	$[S_2O_8^{2-}]_0$, M	$[EtOH]_0/[S_2O_8^{2-}]_0$	Initial rate, M min^{-1}	Yield, %
4.2	0.0314	134	2.05×10^{-4}	
3.9	0.0326	120	2.22×10^{-2}	100
3.5	0.0328	107	2.34×10^{-2}	99
3.1	0.0339	92	2.51×10^{-2}	100
3.1	0.0362	86	2.48×10^{-2}	
2.6	0.0354	74	2.79×10^{-2}	101
2.2	0.0365	60	2.68×10^{-2}	100
2.2	0.0372	59	2.34×10^{-2}	
1.7	0.0374	45	2.50×10^{-2}	100
1.2	0.0392	31	2.76×10^{-2}	98
0.61	0.0403	15	2.00×10^{-2}	93
0.31	0.0415	7.5	1.80×10^{-2}	83
0.16	0.0406	4.0	1.29×10^{-2}	71
0.063	0.0426	1.5	7.96×10^{-3}	
0.013	0.0418	0.31	4.40×10^{-3}	

[a] Further data may be found in ref 8.

The above stoichiometry (eq 3) predicts that 2 mol of monohydrogen sulfate will be produced for every mole of peroxydisulfate reacted. Under some conditions, however, a higher ratio of acid produced to peroxydisulfate reacted was observed; these conditions were the same as those for which the yield of acetaldehyde was less than 100%. Separate experiments[8] showed that the reaction of peroxydisulfate with acetaldehyde to form acetic acid (eq 4) can take place

$$S_2O_8^{2-} + CH_3CHO + H_2O \longrightarrow CH_3CO_2H + 2HSO_4^- \qquad (4)$$

under our conditions. It can be seen that for this reaction 3 mol of titratable acid are produced per mol of peroxydisulfate reacted.

In Table II, data relevant to this point are presented. In this table, 100% yield of total acid represents 2 mol of H^+ released per $S_2O_8^{2-}$ mole used up. It is clear that the deviation from 100% when the ethanol-to-peroxydisulfate ratio is less than 40 represents aldehyde oxidation. The limiting value, based on the complete conversion of ethanol to acetic acid, would be 1.25. Therefore, at low reactant ratios, a significant fraction of ethanol is transformed into acetic acid. A number of experiments[8] in which the initial concentrations of reactants were varied by a factor of four showed that both the "per cent yield total acid" and the initial rates were a function only of the ratio of reactants rather than a function of the individual concentrations.

The important conclusion from the data in Table II and in Figure 2 is that addition of copper ion does

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

TABLE II

PER CENT YIELD OF TOTAL ACID AS A FUNCTION OF ETHANOL-TO-PEROXYDISULFATE RATIO FOR SPONTANEOUS AND COPPER(II)-MODIFIED REACTIONS AT 70°

$[EtOH]_0$, *M*[a]	$([EtOH]_0/[S_2O_8^{2-}]_0)$[a]	Yield[b] total acid, %	Yield[c] total acid, %	Yield[d] total acid, %
3.9	130	100	100	100
3.4	113	100	100	100
2.9	98	100	100	100
2.4	81	101	100	100
1.9	64	100	100	101
1.4	48	101	101	101
0.97	33	101	102	101
0.48	16	103	102	103
0.24	8.1	106	104	105
0.12	4.0	109	109	108
0.097	3.2	111	111	109
0.072	2.4	111	111	111
0.048	1.6	114	114	115
0.024	0.80	117	120	119

[a] $[S_2O_8^{2-}]_0 = 3.0 \times 10^{-2}$ *M* for all runs. [b] No added Cu(II). [c] $[Cu(II)] = 5.0 \times 10^{-5}$ *M*. [d] $[Cu(II)] = 3.0 \times 10^{-4}$ *M*.

not change the stoichiometry. The relative yields of acetaldehyde and acetic acid are independent of the amount of copper ion in the solution, even though, as will be seen below, the rate and rate law are significantly changed. The fact that unchanging absorbance at the isoabsorbtive point (270 nm) as a function of time was observed both in the presence and absence of copper ion also indicates that the stoichiometry is unchanged.

Part A.—The general features of the part A reaction, which occurs when dissolved oxygen is present, are similar to the features of the analogous parts of the 2-propanol[2] and methanol[3a] oxidations. The length of part A increases as the amount of dissolved oxygen increases. When the oxygen present is exhausted, the rate changes dramatically to the much faster part B, during which the oxygen inhibition can be made to reintrude by opening the reaction vessel to air. These phenomena are demonstrated by the curves in Figure 1. Trace metals also affect this part of the reaction. The water solvent had to be carefully purified, as did the sample of $K_2S_2O_8$; in both cases, purification decreased the rate, which is the behavior expected if trace amounts of active metals were present. Addition of EDTA also decreased the rate.

Some variables affecting part A are (1) the peroxydisulfate concentration, (2) the ethanol concentration, (3) the temperature, and (4) the nature and concentration of the metal ion. Both the rate of decrease of peroxydisulfate concentration and the time length τ (the "induction period") for part A can be studied; however, we shall limit the data discussed here to those things which are presently explicable. In Table III, the length of induction period is presented as a function of peroxydisulfate concentration and of temperature. Assuming that the amount of oxygen is the same in all solutions and that the oxygen reacts at every collision with an organic radical (details given below), the disappearance of oxygen should be more rapid (smaller τ) as peroxydisulfate concentration increases and as temperature increases. This is what is observed. The temperature-dependence data make possible a calculation of apparent activation energy; the value obtained from the plot of $1/\tau$ *vs.* $1/T$ is 26 ± 2 kcal mol^{-1}, which is in agreement with the value of 26 ± 1 for the 2-propanol case[2] and 29 ± 2 for the methanol case.[3a] The value of τ increased from 4.0 to 8.0 min as the ethanol concentration decreased from 2.3 to 0.23 *M* ($[S_2O_8^{2-}] = 8.7 \times 10^{-3}$ *M* at 70°). A similar dependence was observed with the other alcohols. With purified reagents and addition of EDTA, the rate of loss of peroxydisulfate is close to that for spontaneous decomposition of $S_2O_8^{2-}$ in pure water.

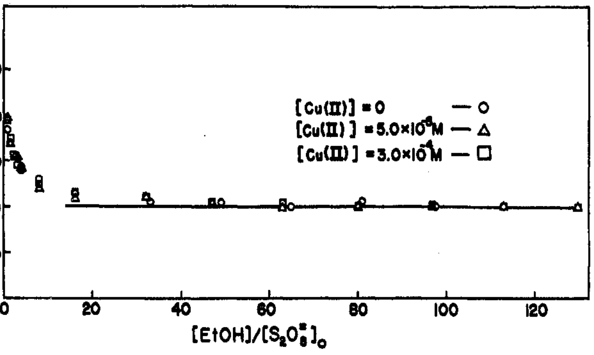

Figure 2.—The yield of total acid (HSO_4^- plus CH_3CO_2H) as a function of the ethanol-to-persulfate ratio for both path B (circles) and path C [triangles and squares for two different concentrations of copper(II) ion].

TABLE III

LENGTH OF THE INDUCTION PERIOD AS A FUNCTION OF PEROXYDISULFATE CONCENTRATION AND TEMPERATURE

Dependence on $[S_2O_8^{2-}]_0$, *M*[a]		Dependence on temp	
$[S_2O_8^{2-}]_0$, *M*[a]	τ, min[b]	Temp, °C	τ, min[a,c]
2.80×10^{-2}	2.0	55	25
1.58×10^{-2}	3.0	60	12
8.27×10^{-3}	5.0	65	7.5
5.72×10^{-3}	7.0	70	5.0
3.42×10^{-3}	7.5	75	3.0
1.96×10^{-3}	9.0	80	2.5
1.49×10^{-3}	10.5		
1.11×10^{-3}	11.5		

[a] $[EtOH]_0 = 1.4$ *M*. [b] At 70°. [c] $[S_2O_8^{2-}]_0 = 8.9 \times 10^{-3}$ *M*.

In Table IV, the influence of Cu(II) concentration on the initial rate of part A, the amount of peroxydisulfate lost in part A, and the length of the induction period τ are presented. The first horizontal row gives ranges of values of these observables found in a number

TABLE IV

EFFECT OF COPPER(II) ON THE RATE OF PART A AT 70°[a]

[Cu(II)], *M*	Initial rate, *M* min^{-1}	$S_2O_8^{2-}$ lost in A, %	τ, min
None	$0.2\text{–}1.8 \times 10^{-4}$	1–2	4.5–5.0
1.0×10^{-8}	1.8×10^{-4}	5.8	5.5
5.0×10^{-8}	1.8×10^{-4}	3.5	6.0
1.0×10^{-7}	3.2×10^{-4}	13	5.6
5.0×10^{-7}	4.5×10^{-4}	23	6.5
1.0×10^{-6}	4.9×10^{-4}	30	6.0
1.5×10^{-6}	5.5×10^{-4}	31	6.5
1.0×10^{-5}	6.2×10^{-4}	43	6.5
2.0×10^{-5}	6.6×10^{-4}	45	6.0
4.0×10^{-5}	6.2×10^{-4}	42	6.5
6.0×10^{-5}	6.6×10^{-4}	44	6.0
8.0×10^{-5}	6.4×10^{-4}	43	6.5
1.0×10^{-4}	6.4×10^{-4}	43	6.5

[a] $[EtOH]_0 = 1.4$ *M*; $[S_2O_8^{2-}]_0 = 8.7 \times 10^{-3}$ *M*.

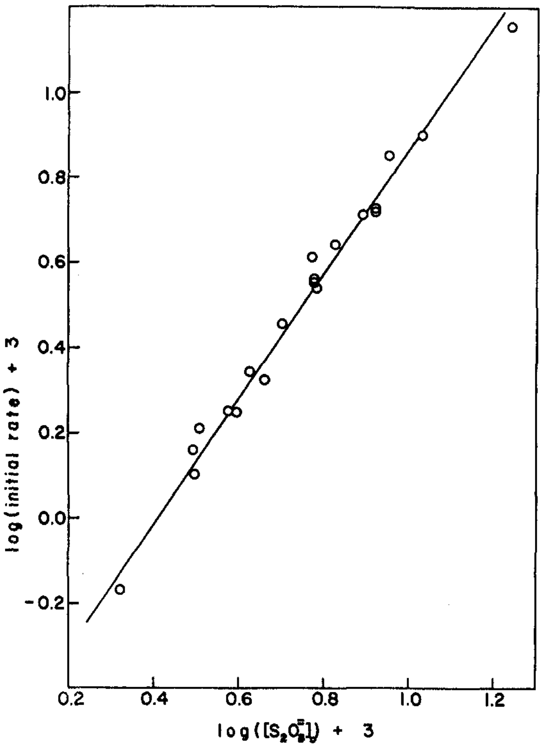

Figure 3.—Data for evaluation of kinetic order (path B) in persulfate concentration. Points are log initial rate against log initial [$S_2O_8^{2-}$]; for [C_2H_5OH] = 1.4 *M*, no added acetaldehyde, and *T* = 70°.

of experiments carried out in the absence of added Cu(II) ion. It is noted that 10^{-8} *M* copper ion has a barely observable effect. The initial rate of reaction (second column) increases with copper concentration, but the rate variation is much smaller than the variation in metal ion concentration. The amount of peroxydisulfate lost in part A also increases with copper concentration, but not in a simple manner. An important observation is the lack of a strong inverse dependence of τ on copper concentration; this indicates that the metal ion does not increase the rate of radical production. Explanations for some of these observations will be given in the Discussion.

Data on the effect of a number of other metal ions on part A of the reaction are given in Table V. Ten metal ions [Ni(II), Fe(II), Cr(III), Hg(II), Sn(II), Sn(IV), Ag(I), Ce(IV), Co(II), and Ti(III)] increase (sometimes marginally) the rate of part A, while five others [Mn(II), Mg(II), Cd(II), Sr(II), and Zn(II)] show no detectable catalytic activity at a level of 10^{-5} *M*. In part, the existence of a redox couple (*e.g.*, $Hg_2^{2+} \rightleftarrows 2\,Hg^{2+} + 2e^-$) seems to be a factor in the catalytic activity; however, the complete explanation must be more complex. No significant influence on the τ values was observed.

Path B.—The oxidation of ethanol by peroxydisulfate in the absence of oxygen and of metal ions follows the stoichiometry mentioned above. The problems uncovered in the order determination have been briefly discussed earlier,[1b] and it was shown there that the oxidation of ethanol is inhibited by the product acetaldehyde when the concentration of aldehyde becomes equal to or larger than 1 × 10^{-3} *M*.

In order to minimize the problem of aldehyde inhibition while determining the order of the reaction, the method of initial rates was employed. The rate was determined as a function of peroxydisulfate concentration at the commencement of part B with the ethanol concentration constant and in large excess. A plot of log (initial rate) against log ([$S_2O_8^{2-}$]$_0$) was made in order to determine the kinetic order; see Figure 3. The slope was 1.52 ± 0.05 (correlation coefficient of 0.990) and hence the order in peroxydisulfate is three halves.

TABLE V

EFFECT OF SOME METAL IONS ON THE RATE OF PART A AT 70° [a]

Metal ion[b]	Initial rate, *M* min^{-1}	$S_2O_8^{2-}$ lost in A, %
Ni(II)	3.2 × 10^{-4}	13
Fe(II)	2.9 × 10^{-4}	10
Cr(III)	5.0 × 10^{-4}	32
Hg(II)	4.5 × 10^{-4}	26
Sn(II)	5.0 × 10^{-4}	33
Sn(IV)	6.5 × 10^{-4}	31
Mn(II)	8.4 × 10^{-5}	5.8
Mg(II)	5.5 × 10^{-5}	4.2
Ag(I)	4.8 × 10^{-4}	26
Ag(I)	1.3 × 10^{-4}	5.7
Ce(IV)	3.2 × 10^{-4}	29
Cd(II)	3.1 × 10^{-5}	2.5
Sr(II)	4.5 × 10^{-5}	3.0
Zn(II)	6.3 × 10^{-5}	4.0
Co(II)	2.5 × 10^{-4}	14
Ti(III)	3.2 × 10^{-4}	16

[a] [EtOH]$_0$ = 1.4 *M*; [$S_2O_8^{2-}$]$_0$ = 8.7 × 10^{-3} *M*. [b] Metal ion concentration is 1.0 × 10^{-5} *M*, except for Ag^+ where it is 1.0 × 10^{-6} *M*.

This method was also used to determine the order in ethanol (see Table VI). The value of $k_{3/2}$ appears to be independent of ethanol concentration and hence the order in ethanol is zero in this concentration range.

TABLE VI

DETERMINATION OF INITIAL RATES OF PATH B AS A FUNCTION OF ETHANOL

[EtOH]$_0$, *M*	[$S_2O_8^{2-}$]$_0$ (B)[a]	Initial rate, *M* min^{-1}	$k_{3/2}$[b]
2.3	7.67 × 10^{-3}	4.78 × 10^{-3}	7.53
2.3	8.15 × 10^{-3}	6.04 × 10^{-3}	8.23
2.0	7.90 × 10^{-3}	5.43 × 10^{-3}	7.75
2.0	7.93 × 10^{-3}	4.92 × 10^{-3}	6.97
1.8	7.84 × 10^{-3}	5.63 × 10^{-3}	8.68
1.8	8.34 × 10^{-3}	4.84 × 10^{-3}	6.34
1.6	8.08 × 10^{-3}	4.50 × 10^{-3}	6.21
1.4	7.88 × 10^{-3}	5.24 × 10^{-3}	7.48
1.1	7.96 × 10^{-3}	4.57 × 10^{-3}	6.47
0.91	8.08 × 10^{-3}	6.18 × 10^{-3}	8.54
0.68	7.96 × 10^{-3}	5.78 × 10^{-3}	8.17

[a] Concentration (*M*) of $S_2O_8^{2-}$ at initiation of part B; note the essential constancy. [b] Units are $M^{-1/2}\,min^{-1}$.

The rate law for path B is

$$-d[S_2O_8^{2-}]/dt = k_{3/2}[S_2O_8^{2-}]^{3/2}$$

Confirmation of this is seen in Figure 4 which is a typical integrated rate plot covering 89% reaction.

The apparent activation energy for path B was determined from the values of $k_{3/2}$ at 55, 60, 65, 70, 75, and 80° to be found in the middle column of Table VII. A linear Arrhenius plot was obtained (correlation coefficient 0.993) with a slope corresponding to an activation energy of 17.2 ± 0.8 kcal mol^{-1}.

TABLE VII

SUMMARY OF RATE CONSTANTS FOR PATH B AND PATH C AS A FUNCTION OF TEMPERATURE

Temp, °C	$k_{3/2}$, $M^{-1/2}$ min^{-1}[b]	$k'_{3/2}$, $M^{-1/2}$ min^{-1}[c]
55	2.30	
60	3.88	70.3
65	5.97	116
70	8.48	177
75	11.0	288
80	16.1	393

[a] $[S_2O_8^{2-}]_0(B) = 1.0 \times 10^{-2}$ *M*; $[EtOH]_0 = 1.4$ *M*. [b] Reaction in absence of Cu(II); *i.e.*, path B. [c] $[Cu(II)] = 5.0 \times 10^{-5}$ *M*; *i.e.*, path C.

Path C.—In our initial experiments, it was found that rates in part B of the reaction were not significantly influenced by small amounts of EDTA (ethylenediaminetetraacetic acid); therefore, catalysis by adventitious metal ions was not considered important. However, further investigation showed that copper(II) ion at concentrations of 10^{-5} *M* or higher changed the kinetic behavior without dramatically increasing the rate. A similar effect of copper(II) had been noted in the methanol oxidation.[3a] This was interesting because part B of the 2-propanol system was not influenced by any of the metal ions tried.[2] This basic difference suggested that a study of the behavior of copper(II) in the ethanol oxidation would be worthwhile.

It should be noted that metal ions may enter into a chain reaction and not change the rate appreciably but change the mechanism significantly. This was found to be the case here. For this reason the reaction in the presence of copper(II) might better be called "the copper(II)-modified mechanism" rather than "the copper(II)-catalyzed mechanism." For the sake of simplicity, however, it will be called path C. In a series of kinetic runs, the concentration of copper(II) was varied over a factor of 50,000 in order to determine in which fashion the metal ion modifies the mechanism. Some results are presented in Table VIII. At concentrations of 10^{-6} *M* or lower, the rate was about the same as in the absence of metal ion. At concentrations of 10^{-5} *M* or higher, the rate is more rapid and increases with increasing copper concentration.

TABLE VIII

VARIATION IN RATE COEFFICIENTS WITH VARIATION IN COPPER(II) CONCENTRATION FOR PATH AT 70°

[Cu(II)], *M*	$[EtOH]_0$ *M*	$[S_2O_8^{2-}]_0(B)$, *M*	$R_{3/2}$[a]	R_1[b]
5.1×10^{-4}	1.1	6.85×10^{-3}	22.3	1.73
1.5×10^{-4}	1.1	6.43×10^{-3}	30.0	1.98
1.0×10^{-4}	1.1	6.20×10^{-3}	20.6	1.28
5.0×10^{-5}	1.4	5.00×10^{-3}	21.9	1.29
5.1×10^{-5}	1.1	6.25×10^{-3}	18.3	1.08
1.0×10^{-5}	1.1	5.87×10^{-3}	13.3	0.793
1.0×10^{-5}	1.4	5.10×10^{-3}	14.8	0.868
1.5×10^{-6}	1.4	6.00×10^{-3}	9.32	0.601
1.0×10^{-6}	1.4	6.10×10^{-3}	9.17	0.574
1.0×10^{-6}	1.4	6.46×10^{-3}	8.02	0.522
5.0×10^{-7}	1.4	6.77×10^{-3}	9.25	0.626
1.0×10^{-7}	1.4	7.63×10^{-3}	8.55	0.591
5.0×10^{-8}	1.4	8.40×10^{-3}	7.79	0.575
1.0×10^{-8}	1.4	8.18×10^{-3}	9.32	0.632

[a] Units are $M^{-1/2}$ min^{-1}, assuming three-halves order in $S_2O_8^{2-}$. [b] Units are min^{-1}, assuming first order in $S_2O_8^{2-}$.

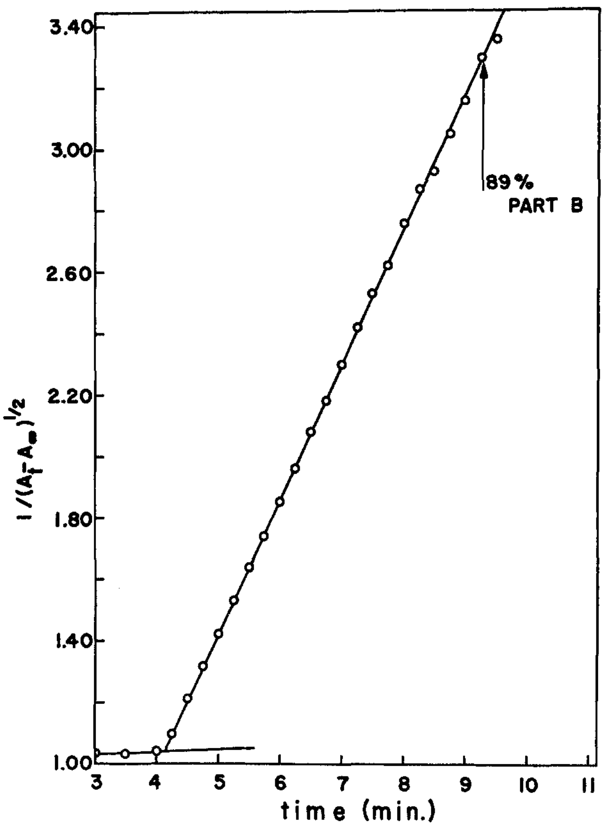

Figure 4.—A typical $^3/_2$-order integrated plot for path B; $[S_2O_8^{2-}]_0 = 1.0 \times 10^{-2}$ *M*, $[C_2H_5OH] = 1.4$ *M*, and $T = 70°$.

In view of the fact that chain mechanims such as are seen in the present reaction are not additive (see Discussion), the assumption that path C is dominant when the copper concentration is greater than 10^{-5} *M* was made. The internal consistency of the results below indicates that the assumption is probably valid.

Path C was found to be first order in peroxydisulfate. The rate coefficient R_1 was evaluated over an eightfold concentration range (see Table IX) and the value is constant. Further, plots using the integrated first-order rate equation were linear to between two and three half-lives. A typical plot is shown in Figure 5. Path C was found to be zero order in ethanol; the results are shown in Table X. In this copper-modified mechanism, it was found[8] that product aldehyde does not act as an inhibitor as it does in the path B mechanism.

TABLE IX

VARIATION OF RATE COEFFICIENT WITH PEROXYDISULFATE CONCENTRATION AT CONSTANT ETHANOL AND COPPER(II) CONCENTRATIONS[a]

$[S_2O_8^{2-}]_0(B)$, *M*	R_1, min^{-1}	$[S_2O_8^{2-}]_0(B)$, *M*	R_1, min^{-1}
2.80×10^{-2}	1.40	1.10×10^{-2}	1.42
2.38×10^{-2}	1.33	8.27×10^{-3}	1.51
1.58×10^{-2}	1.45	6.57×10^{-3}	1.29
1.43×10^{-2}	1.42	5.72×10^{-3}	1.54
1.16×10^{-2}	1.35	3.42×10^{-3}	1.41
1.14×10^{-2}	1.34		

[a] $[EtOH]_0 = 1.4$ *M*; $[Cu(II)] = 5.0 \times 10^{-5}$ *M*; at 70°.

The order in copper(II) ion for path C was found to be one-half. The copper(II) concentration was varied over a factor of 5 and the observed first-order rate

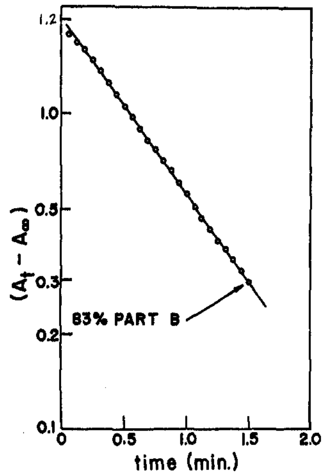

Figure 5.—A typical first-order integrated plot for path C; $[S_2O_8^{2-}]_0 = 1.5 \times 10^{-2}\ M$, $[C_2H_5OH] = 1.4\ M$, $[Cu^{2+}] = 5.0 \times 10^{-5}\ M$, and $T = 70°$.

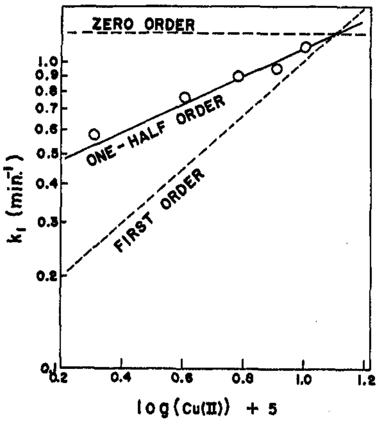

Figure 6.—The dependence of the pseudo-first-order rate constant on $[Cu^{2+}]$ for path C; $[S_2O_8^{2-}]_0 = 2.5 \times 10^{-2}\ M$, $[C_2H_5OH] = 2.3\ M$, and $T = 60°$.

TABLE X

VARIATION OF RATE COEFFICIENT WITH ETHANOL CONCENTRATION AT CONSTANT PEROXYDISULFATE AND COPPER(II) CONCENTRATIONS[a]

$[EtOH]_0$, *M*	$[S_2O_8^{2-}]_0(B)$, *M*	R_1, min^{-1}
1.8	5.12×10^{-3}	1.36
1.6	4.82×10^{-3}	1.52
1.4	4.74×10^{-3}	1.23
1.1	4.74×10^{-3}	1.52
0.91	4.71×10^{-3}	1.55
0.68	4.82×10^{-3}	1.36
0.46	4.96×10^{-3}	1.55
0.23	5.17×10^{-3}	1.23
0.091	5.83×10^{-3}	1.21

[a] $[Cu(II)] = 5.0 \times 10^{-5}\ M$; at 70°.

constants appear to be dependent upon the copper(II) ion concentration to the one-half power (see Figure 6). The rate law for part C is, at least over a limited range, therefore

$$\text{rate} = k_{3/2}'[S_2O_8^{2-}][Cu(II)]^{1/2}$$

It should be noted that all kinetic runs in the study of path C were done at or above an ethanol-to-peroxydisulfate ratio of 40, so that the yields of aldehyde in all cases should be 100 ± 1%, as in Figure 2.

The apparent activation energy for path C was determined from kinetic runs at five temperatures (see last column in Table VII). A linear Arrhenius plot was obtained (correlation coefficient = 0.996) with a slope corresponding to an activation energy of 20.2 ± 0.8 kcal mol^{-1}.

In order to find out if the Cu(II) ion changes oxidation state during the course of the reaction, several experiments were carried out, as follows. Copper(II) ion in aqueous solution has an extinction coefficient of 390 M^{-1} cm^{-1} at 228 nm and 70°; consequently, there is a significant absorbance at high copper(II) concentrations ($1.00 \times 10^{-3}\ M$). If one performs a kinetic run at this copper(II) concentration (such that the only absorbing species are peroxydisulfate and copper) and if copper(II) undergoes no chemical change, the absorbance at infinite time should be due to copper(II) alone. On performing such a kinetic run and using the extinction coefficient of copper(II) the absorbance at time infinity was predicted well within experimental error (±2%), indicating that copper(II) has undergone no net chemical change.

The second experiment was carried out to show that the expression below is valid. Two runs at $[Cu(II)] = 1 \times 10^{-3}\ M$ were made. In the first run, the same concentration of copper(II) was put in both the sample and reference cells. In the second run, copper(II) was put only in the sample cell. If the expression in question is valid, the absorbance in the first run should be due to persulfate alone. Initial rates and rate constants were calculated from both runs, assuming in the second run that the expression in question was valid and the concentration of persulfate calculated assuming that all the copper(II) still existed mainly in the plus two state. The rate constants agreed within experimental error (±5%) indicating that the equation is valid.

$$[Cu(II)]_{\text{added}} - [Cu(II)]_{\text{during run}} \simeq 0$$

It seemed worthwhile to find out if other metal ions had comparable effects to copper(II). Considerable scatter in the rate constant values were obtained in these experiments, but no significant alteration in rate was observed except for the cases of Ag(I) and $(NH_4)_6Mo_7O_4$. The silver acted as a catalyst, as expected,[11] but only when increased in concentration to $10^{-4}\ M$. The molybdate acted as an inhibitor; the observed rate was lower by a factor of two when the molybdate salt concentration was $10^{-5}\ M$. The reason for this inhibition is not understood.

Discussion

Comparison of Rates.—Before proceeding with the discussion of mechanism, it is helpful to make a summary of the relative rates of the various paths involved (see Table XI). These relative rates are based on the rates of the spontaneous thermal decomposition of peroxydisulfate[10,11] as unity. The rate in part A, in some runs, was essentially identical with the basis rate. For path B, the chain length (as given by the

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[11] (a) W. K. Wilmarth and A. Haim in "Peroxide Reaction Mechanisms," J. O. Edwards, Ed., Wiley-Interscience, 1962, p 204; (b) D. A. House, *Chem. Rev.*, **62**, 185 (1962); (c) E. J. Behrman and J. E. McIsaac, Jr., in "Mechanisms of Sulfur Reactions," Vol. 2, N. Kharasch, Ed., Interscience, Los Angeles, Calif., 1968, p 193.

TABLE XI

COMPARISON OF RELATIVE REACTION RATES (CHAIN LENGTH) OF VARIOUS PATHS STUDIED (70°)

Alcohol	Alcohol concn	$[S_2O_8^{2-}]$, M	[Cu(II)], M	Part of reaction	k_1, min^{-1}	Initial rate, M min^{-1}	Rel rate[a,d]
					1.45×10^{-3}[a]		1
EtOH	1.4	1.0×10^{-2}		A		1.30×10^{-5}[b]	1
EtOH	1.4	1.0×10^{-2}		B		8.60×10^{-3}	590
EtOH	1.4	8.7×10^{-3}	1.0×10^{-5}	A		6.4×10^{-4}	51[c]
EtOH	1.4	1.0×10^{-2}	5.0×10^{-5}	C			870
CF_3CH_2OH	1.3	9.36×10^{-3}				5.91×10^{-5}[e]	4.3

[a] References 4, 10, and 11. The value of relative rate may be defined as the chain length under the conditions of the experiment. The chain length for this reaction is dependent on concentrations. [b] See General under Results. [c] See Table IV. [d] Defined by the relative rate of loss of peroxydisulfate under the conditions. [e] After correction for spontaneous thermal decomposition.

relative rate) is about 600; this value falls between those for methanol (about 50)[3] and 2-propanol (about 1800).[2] The relative rates for path B and path C are not greatly different, but, as mentioned above and discussed below, there is a definite change in the kinetics.

Included in Table XI is the rate of oxidation of 2,2,2-trifluoroethanol.[8] The powerful electron-withdrawing effect of the trifluoromethyl group appears to have an enormous retarding effect upon the rate of loss of peroxydisulfate, decreasing it to only four times the rate of the spontaneous thermal decomposition. The rate of oxidation of ethanol under these same conditions is about 140 times faster.

Evidence for Free Radical Nature.—The evidence for the free radical nature of the mechanisms of the oxidation of various alcohols is vast and has been commented on in many articles and reviews.[2–8,10] In the course of our work, we found no reason to doubt this general conclusion. For example, we observed the following: (a) inhibition by oxygen gas, and marked increase in rate at the time of oxygen disappearance, (b) inhibition by allyl acetate and allyl alcohol, (c) fractional orders in the rate laws, (d) inhibition by product aldehyde, and (e) change in kinetic pattern and rate on addition of copper(II) ion. All of these phenomena are characteristic of free radical chain reactions. We shall, therefore, postulate mechanisms of this type.

Chain Initiation Step.—The apparent discrepancy mentioned in the introduction between the allyl acetate experiments[4] and the tentative rate laws[3b,4] was first pointed out by Kolthoff, Meehan, and Carr,[4] although not resolved at that time. The difficulty, essentially, is that the allyl acetate experiments indicate that chain initiation is occurring by way of the unimolecular initiation step (eq 2) while the overall second-order nature of the tentative rate law, which as reported was

$$-\mathrm{d}[S_2O_8^{2-}]/\mathrm{d}t = k[S_2O_8^{2-}]^{3/2}[RCH_2OH]^{1/2} \qquad (R = CH_3 \text{ or } H)$$

indicates that initiation is occurring by way of the bimolecular initiation step (eq 1). It is to be noted, however, that the early kinetic experiments were carried out in the concentration ranges where aldehyde is now known to be an inhibitor.[1b,8] Further, it has been observed here that the rate appears to be a function of the ethanol concentration when the yields of aldehyde are less than 100%. These observations suggest that the apparent half-order dependence on alcohol concentration in the second-order rate law is related to the aldehyde inhibition. The results would be explicable if there is a competition between ethanol and acetaldehyde for the very reactive sulfate radical ion; the competition steps would be

$$SO_4\cdot^- + CH_3CH_2OH \xrightarrow{k_{2a}} HSO_4^- + CH_3\dot{C}HOH$$

$$SO_4\cdot^- + CH_3CHO \longrightarrow HSO_4^- + CH_3\dot{C}O$$

Under conditions where $[CH_3CH_2OH] \gg [CH_3CHO]$, the ethanol would compete successfully and any aldehyde inhibition would be minimized. Therefore, the order in ethanol which is observed at high concentrations of ethanol would be the true order. As seen in Table VI, this order is zero. We conclude that the proper rate law for part B of the reaction is

$$\text{rate} = k_{3/2}[S_2O_8^{2-}]^{3/2}$$

and that the unimolecular initiation step k_{1a} is the correct one. The apparent discrepancy is therefore resolved.

Recently, the evidence for a unimolecular initiation step in the oxidation of a number of organic compounds has been supported by the careful studies of Crematy[12] on oxidation of organic detergents by peroxydisulfate.

Path B. Mechanism.—The mechanism of the reaction in the absence of either oxygen or copper can now be formulated. The proposed steps are k_{1a}, k_{2a}, and

$$CH_3\dot{C}HOH + S_2O_8^{2-} \xrightarrow{k_{3a}} CH_3CHO + HSO_4^- + SO_4\cdot^-$$

$$2CH_3\dot{C}HOH \xrightarrow{k_{4a}} CH_3CHO + CH_3CH_2OH$$

$$H_2O + CH_3CHO \rightleftharpoons CH_3CH(OH)_2$$

The first step (constant k_{1a}) is the unimolecular homolytic scission of the peroxydisulfate ion. The second step (constant k_{2a}), which is the abstraction of a hydrogen atom on the carbon having a hydroxyl group, is analogous to the second step in the 2-propanol and methanol oxidations. The rate constants for these hydrogen atom abstractions have recently been measured[13] and found to be very large. Little is known of the third step (k_{3a}), but it is a reasonable one and it fits both stoichiometry and kinetics. The type of termination step (k_{4a}) is demanded by the kinetics, it is consistent with the absence of 2,3-butanediol, and it has recently been reported[14] in the photolytic oxidation of ethanol by hydrogen peroxide. The final step is the known, rapid hydration equilibrium of acetaldehyde. Upon application of the steady-state approximation and neglect of the term due to the

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(12) E. P. Crematy, Ph.D. Thesis, University of Sydney, Australia, 1970.

(13) L. Dogliotti and E. Hayon, *J. Phys. Chem.*, **71**, 2511 (1967).

(14) J. Barrett, A. L. Mansell, and R. J. M. Ratcliffe, *Chem. Commun.*, 48 (1968).

spontaneous thermal decomposition of peroxydisulfate, the following rate law is obtained.

$$-d[S_2O_8^{2-}]/dt = k_{3a}(k_{1a}/k_{4a})^{1/2}[S_2O_8^{2-}]^{3/2}$$

This is consistent with the observed rate law. In view of the fact that $SO_4\cdot^-$ reacts directly with alcohols,[13] there is no need to postulate the intermediacy of hydroxyl radicals $OH\cdot$.

It is a necessary condition of such a chain mechanism that the observed activation energy be greater than one-half the activation energy (33.5 kcal mol^{-1}) of the initiation step. The values are 17.2 and 16.7, respectively; the difference is small and in the proper direction. We conclude that the chain propagation step k_{3a} has a very small activation energy.

When acetaldehyde is present in kinetically significant amounts, the mechanism must be modified to include appropriate steps. For several reasons, the most important of which is the obvious activation of α-hydrogen extraction by hydroxyl groups, we feel that the hydrate form of the aldehyde is the reactive form. The new steps are

$$SO_4\cdot^- + CH_3CH(OH)_2 \xrightarrow{k_{2b}} HSO_4^- + CH_3\dot{C}(OH)_2$$

$$CH_3\dot{C}(OH)_2 + S_2O_8^{2-} \xrightarrow{k_{3b}} CH_3CO_2H + HSO_4^- + SO_4\cdot^-$$

$$CH_3\dot{C}(OH)_2 + CH_3\dot{C}HOH \xrightarrow{k_{4b}} \text{termination products}$$

These three steps plus the k_{1a}, k_{2a}, and k_{3a} steps mentioned above provide a derived rate law which is consistent with the observations concerning aldehyde inhibition. Since this type of inhibition has been adequately discussed elsewhere,[1b,3a,8] further discussion on aldehyde inhibition is not deemed necessary.

Path C. Mechanism—The influence of copper ion on the kinetics turns out to be readily analyzed. The rate law is

$$\text{rate} = k_{3/2}'[S_2O_8^{2-}][Cu(II)]^{1/2}$$

Therefore, since the overall order is $^3/_2$ and the τ values do not depend on [Cu(II)], the initiation step is again k_{1a}. The data in Table II, along with much other data reported elsewhere,[8] show that the copper ion does not influence the stoichiometry. Since the product distribution between acetaldehyde and acetic acid is not a function of [Cu(II)], one can conclude that copper ion does not enter at the k_2 stage. The copper(II) must, therefore, react with the organic radicals formed in the k_2 stage.

The postulated mechanism for path C is then k_{1a}, k_{2a}, and the new steps

$$CH_3\dot{C}HOH + Cu(II) \xrightarrow{k_5} CH_3CHO + H^+ + Cu(I)$$

$$Cu(I) + S_2O_8^{2-} \xrightarrow{k_6} Cu(II) + SO_4^{2-} + SO_4\cdot^-$$

$$Cu(I) + CH_3\dot{C}HOH \xrightarrow{k_7} Cu(O) + CH_3CHO + H^+$$

$$Cu(O) + S_2O_8^{2-} \xrightarrow{k_8} Cu(II) + 2SO_4^{2-}$$

Step k_{1a} is again initiation, steps k_{2a}, k_5, and k_6 are the propagation steps, and k_7 is the new termination. Using the steady-state approximation for concentrations of $SO_4\cdot^-$, $CH_3\dot{C}HOH$, Cu(0), and Cu(I), the rate law

$$\text{rate} = (k_{1a}k_5k_6/k_7)^{1/2}[S_2O_8^{2-}][Cu(II)]^{1/2}$$

is obtained; this derived law is in agreement with the observed law. The observed activation energy 20.2 kcal mol^{-1} also is consistent with expectations for it is less than E_a for the k_{1a} step but greater than half of that value.

In view of the fact that aldehyde is oxidized to acid in the presence of copper ion, other steps involving $CH_3\dot{C}(OH)_2$ and Cu(II), etc., could be postulated. There appears no necessity for doing so. One point is, nevertheless, important. Since the termination step no longer involves the aldehyde radical $CH_3\dot{C}(OH)_2$, inhibition by aldehyde is not expected. Within our experimental error, no influence of acetaldehyde on the rate of path C was observed.

Part A.—The results obtained for part A are explicable in terms of oxygen inhibition and its consequences. We feel, however, that lengthy discussion here is unwarranted as the general behavior of part A has been developed in earlier papers.[2,3a] Suffice it to say that steps k_{1a} and k_{2a} are followed by the step

$$O_2 + CH_3\dot{C}CHOH \longrightarrow \cdot OOC(CH_3)HOH$$

or its kinetic equivalent

$$O_2 + CH_3\dot{C}HOH \longrightarrow HO_2\cdot + CH_3CHO$$

Recombination of peroxy radicals can then occur to terminate the chain at short chain length. This provides an entirely satisfactory explanation of the rate inhibition by oxygen gas.

Interconnection of Reactions.—The continuing problem of interpretation of the mechanisms of peroxydisulfate ion oxidations can be attributed, in part, to the implicit, but often employed, assumption that the mechanisms of these reactions are independent. For example, it has been felt that the oxidation of water will go on in the presence of alcohols in the same way that it goes in their absence. Also, it has been assumed that the alcohol oxidation can be treated identically when aldehyde is present as when it is absent. The invalidity of the assumption can be clearly recognized in one experimental result, namely, the inhibition of the oxidation of ethanol when acetaldehyde is present. If the product aldehyde were being oxidized independently, then the rate of disappearance of peroxydisulfate would of necessity be greater, rather than smaller. Even if alcohol and aldehyde compete for the sulfate radical ions, the rate of disappearance of peroxydisulfate must still be greater when the aldehyde is present. The fact that there is inhibition can only be explained if the termination step for the ethanol oxidation is altered when aldehyde is present.

Registry No.—Cu(II), 15158-11-9; Ni(II), 14701-22-5; Fe(II), 15438-31-0; Cr(III), 16065-83-1; Hg(II), 14302-87-5; Sn(II), 22541-90-8; Sn(IV), 22537-50-4; Mn(II), 16397-91-4; Mg(I), 14581-92-1; Mg(II), 22537-22-0; Ag(I), 14701-21-4; Ce(IV), 16065-90-0; Cd(II), 22537-48-0; Sr(II), 22537-39-9; Zn(II), 23713-49-7; Co(II), 22541-53-3; Ti(III), 22541-75-9; ethanol, 64-17-5; peroxydisulfate ion, 15092-81-6.

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