The Kinetics and Mechanisms of the Oxidation of Methanol and of α-Phenylethanol by Peroxydisulfate Ion[1]

JOHN E. MCISAAC, JR., AND JOHN O. EDWARDS

Metcalf Chemical Laboratories, Brown University, Providence, Rhode Island 02912

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The oxidation of methanol by aqueous peroxydisulfate ion has been found to proceed *via* two distinct paths, one in the presence of oxygen (path A), the other in its absence (path B). The reaction path in absence of oxygen was found to be catalyzed by Cu(II) ion and inhibited by the oxidation product, formaldehyde. When copper catalysis and formaldehyde inhibition are minimized the observed rate law is rate = $k[S_2O_8^{2-}]^{3/2}$. A radical-chain mechanism consistent with the observed rate law and stoichiometry is presented. A value of k for the oxidation of methanol-d_3 was determined. The isotope effect is shown to be reasonable with respect to the proposed mechanism. Additional steps are presented to explain the formaldehyde inhibition. Rate and stoichiometric data are also presented for the peroxydisulfate oxidation of α-phenylethanol.

The kinetics of the oxidation of methanol by aqueous peroxydisulfate ion have been reinvestigated. Previous investigators[2-7] had proposed that the oxidation proceeds by a radical-chain mechanism. They were unable to suggest a mechanism consistent with their observed rate dependence (three-halves on peroxydisulfate and one-half on methanol) without involving a bimolecular initiation step between peroxydisulfate and methanol. Kolthoff,[2] however, using allyl acetate as a radical trapping agent, had shown that a bimolecular step does not contribute to chain initiation. This investigation was undertaken to clarify this situation and to investigate further other factors (such as the reported effects of trace metals and oxygen) affecting the peroxydisulfate oxidation of alcohols.

Experimental Section

Materials.—All chemicals not described below were reagent grade. The solvent in all cases was unbuffered; the pH varied from approximately 3.5 to 2 in the runs with methanol. Unless indicated otherwise, all experiments involving methanol were performed using distilled water. Deionized water, prepared by passing distilled water through a Barnsted mixed-bed ion-exchange column, was used for the experiments with α-phenylethanol.

Baker and Adamson reagent grade potassium peroxydisulfate was recrystallized from deionized water either once or twice before use. Spectral grade methyl alcohol (Fisher Analyzed Reagent No. A-408) was used in the majority of experiments. A few runs were carried out with reagent grade methanol distilled from calcium oxide; no differences were found between the rate constants obtained with the two grades of alcohol. Methanol-free formaldehyde was prepared by the method of Ledbury and Blair.[8] The aqueous formaldehyde solution was analyzed for per cent formaldehyde. This value, coupled with the measured index of refraction of the solution, was then applied to a ternary phase diagram[9] for the system methanol–formaldehyde–water. For a typical preparation which was 25%, w/w, in formaldehyde with $n^{18}D$ 1.3593, the indicated percentage of methanol is 0 ± 2. Allyl acetate, purchased from the Aldrich Chemical Co., was freshly distilled before use, bp 101.5–102°.

Methanol-d_3 (>99% isotopic purity claimed by supplier) was purchased from Merck Sharp and Dohme of Canada, lot no. AP 569, and used without further purification. Mass spectral and infrared analyses showed its isotopic purity to be 96% or greater.

K & K Laboratories α-phenylethanol was fractionally distilled before use, bp 89–90° (12 mm), $n^{20}D$ 1.5213. Tlc on 0.5-mm-thick silica gel plates in 4:1 v/v benzene–ethyl acetate gave only one spot with an R_f value of 0.41.

Techniques.—Kinetics were followed on a Beckman DK-1 recording spectrophotometer. A thermostated cell holder through which water or ethylene glycol was circulated from a constant-temperature bath enabled temperatures within the cell compartment to be maintained to ±0.5°. Matched ground-glass stoppered silica cells of 1.0-cm path length were used.

Peroxydisulfate ion absorbs in a broad ascending curve from approximately 300 mμ out to beyond 200 mμ.[10] This fact in conjunction with the nonabsorbing character of methanol and formaldehyde in this region of the spectrum allowed the loss of peroxydisulfate ion to be followed with full-scale deflection over a wide range of concentrations. In the case of α-phenylethanol, kinetics were monitored by following the increase in absorption due to the product acetophenone (log $E_{\max}^{55°}$ 4.074, $\lambda_{\max}$ 244 mμ). In all cases the reference solution was of the same composition as the reaction mixture, with the omission of peroxydisulfate. Previous work[7] and preliminary experiments showed that for the concentrations of peroxide employed the spectrophotometer light source does not induce the photochemical decomposition of peroxydisulfate.

Rate constants were calculated either from plots of $1/(A_t - A_\infty)^{1/2}$ *vs.* time, where A_t is absorbance at time t and A_∞ is absorbance at time infinity (ten half-lives) or directly from spectrophotometric traces. A_∞ was not usually zero; it varied from zero by ±0.03 units owing to slight cuvette imbalance and/or instrument drift. Rate constants calculated for duplicate runs usually agreed to ±8%. Initial rate constants varied by ±20%; in these cases at least seven determinations were made and an average taken.

Three different procedures were employed for initiating the reactions depending upon the desired degree of oxygen exclusion. When the exclusion of air was not required, the procedure was to allow the peroxydisulfate solution to attain temperature in the cell in the spectrophotometer. Alcohol and/or other additives were then introduced directly into the cell with a hypodermic syringe or micropipet, and the solution was mixed by shaking; this procedure usually required from 10 to 20 sec. In those runs which were carried out in order to determine initial rate constants, it was desirable to reduce the amount of air present in the reaction mixture. In these cases deaeration was accomplished by bubbling a stream of prepurified nitrogen, for approximately 0.5 hr, through a peroxydisulfate solution in an external vessel fitted with a rubber stopper drilled to pass a small pipet. The solution was then brought to temperature and pipeted into the spectrophotometer cell where other reactants were added in the manner described above. An apparatus was designed for the purpose of carrying out a number of runs in an environment as free from oxygen as possible. This apparatus and the method of initiating the reaction were similar to that previously described.[7] In the experiments involving allyl acetate, the production of

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[1] Abstracted from the Ph.D. Thesis of J. E. McIsaac, Jr., Brown University, 1968. A preliminary account of this work has been published: J. O. Edwards, A. R. Gallopo, and J. E. McIsaac, Jr., *J. Amer. Chem. Soc.*, **88**, 3891 (1966).

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

[3] P. D. Bartlett and J. D. Cotman, *ibid.*, **71**, 1419 (1949).

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

[5] L. R. Subbaraman and M. Santappa, *Proc. Indian Acad. Sci.*, **64**, 345 (1966).

[6] L. R. Subbaraman and M. Santappa, *Z. Phys. Chem.*, **48**, 163 (1966).

[7] D. L. Ball, M. M. Crutchfield, and J. O. Edwards, *J. Org. Chem.*, **25**, 1599 (1960).

[8] W. Ledbury and E. Blair, *J. Chem. Soc.*, 26 (1925).

[9] J. F. Walker, "Formaldehyde," 3rd ed, Reinhold Publishing Corp., New York, N. Y., 1953, p 484.

[10] L. J. Heidt, J. B. Mann, and H. R. Schneider, *J. Amer. Chem. Soc.* **70**, 3011 (1948).

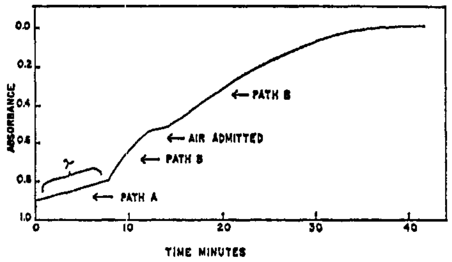

Figure 1.—Typical trace of absorbance *vs.* time at 231 mμ showing path A, path B, and the length of path A, τ.

polyallyl acetate precluded the use of a spectrophotometric technique. The method employed was iodometric analysis of unreacted peroxydisulfate.[11]

Yields.—Yields of formaldehyde were determined by sealing the reactants in 5-ml glass ampoules and submerging the ampoules in a thermostated bath for the required length of time, after which they were analyzed by the method of Romijin.[12] The yields of acid produced during the course of the reaction were determined similarly except that aliquots were titrated with 0.1 *N* NaOH using an automatic titrator, a Radiometer titragraph, type SBR2C. The remaining solution was analyzed spectrophotometrically for the concentration of unreacted peroxydisulfate.

Results

Methanol Oxidation.—The oxidation of methanol was found to proceed *via* two distinct reaction paths. When the oxidation is initiated in a stoppered spectrophotometer cell with reactants initially at equilibrium with the atmosphere, a relatively slow reaction is first observed; after several minutes, however, the reaction rate increases dramatically. If a small amount of air is introduced into the cuvette, the rapid reaction is immediately quenched and the rate of loss of peroxydisulfate returns to approximately the initially observed value. Again, after a short time a sharp rate increase is observed.

Figure 1 illustrates these dramatic changes. The slower portion of the reaction will be designated as path A, the fast portion as path B, and the length of path A will be τ; this nomenclature is the same as that chosen by Ball, *et al.*, who observed these same general characteristics in the peroxydisulfate oxidation of 2-propanol.[7] The rapid change in the slopes of plots of absorbance *vs.* time, from path A to path B, probably coincides with the complete consumption of dissolved oxygen in the system. Inhibition of peroxydisulfate oxidations involving organic reductants by oxygen is is well documented.[4-7,13,14] Attempts to eliminate completely the A portion of the reaction by degassing all reactants with oxygen-free nitrogen and carrying out the reactions in a nitrogen atmosphere were unsuccessful. τ could only be shortened by slightly more than a factor of one-half, to 3.5 min, under conditions for which without degassings, τ averaged 8 min. This is reasonable since oxygen is continually produced by the peroxydisulfate oxidation of water.[15] Some oxygen would then always be present at the initiation of the alcohol oxidation. No significant difference was observed in the shape of the three-halves-order plot or the value of the rate constant obtained under nitrogen as compared to the results found by the technique usually employed.

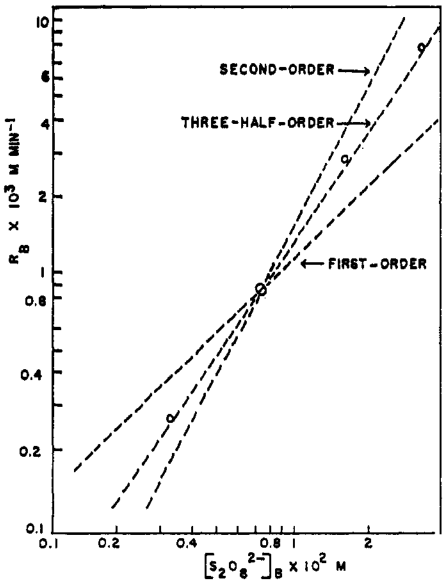

Figure 2.—Demonstrating the kinetic dependence of path B on the concentration of $S_2O_8^{2-}$ at the commencement of path B: $T = 70°$; $[CH_3OH]_0 = 0.78$ *M*; R_B = initial rate of loss of $S_2O_8^{2-}$.

For the purposes of the presentation of tabular and graphical data, initial reactant concentrations, indicated by the subscript zero, are those at the beginning of path A. The subscripts A and B will also be used when it is necessary to differentiate between initial reactant concentrations for the two paths.

Stoichiometry.—The previously observed stoichiometry (when $[CH_3OH]_0 \geq 1$ *M*) given by eq 1 was reaffirmed; see Table I. Equation 2 is included to demonstrate the hydration equilibrium of formaldehyde; under the conditions of our experiments formaldehyde is present at >99% as the hydrate.[16]

$$S_2O_8^{2-} + CH_3OH \longrightarrow CH_2O + 2H^+ + 2SO_4^{2-} \quad (1)$$

$$CH_2O + H_2O \rightleftharpoons CH_2(OH)_2 \quad (2)$$

Table I

Yield of Formaldehyde as a Function of Methanol Concentration and Temperature[a,b]

$[CH_3OH]_0$, *M*	Temp, °C 60	70	80
1.5	101.0	101.8	102.7
1.1	100.4	101.0	99.4
0.78	96.4	98.0	100.8
0.39	93.7	95.6	98.1
0.20	88.6	91.0	87.0

[a] Yields of H_2CO in per cent, based on $K_2S_2O_8$ lost at initial $K_2S_2O_8$ concentrations of approximately 8.5×10^{-3} *M*, assuming the stoichiometry of eq 1. [b] Yields >100% are due to interference by methanol in the analytical method at concentrations of methanol >0.8 *M*.

Rate Law. Path B.—The rate of loss of peroxydisulfate ion for path B was found to be proportional to the

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[11] I. M. Kolthoff and E. M. Carr, *Anal. Chem.*, **25**, 298 (1953).

[12] I. M. Kolthoff and N. H. Furman, "Volumetric Analysis," Vol. 2, John Wiley & Sons, Inc., New York, N. Y., 1929, p 444.

[13] A. R. Gallopo, Ph.D. Thesis, Brown University, 1967.

[14] H. N. Po and T. L. Allen, *J. Amer. Chem. Soc.*, **90**, 1127 (1968); E. Ben-Zvi and T. L. Allen, *ibid.*, **83**, 4352 (1961); A. J. Kalb and T. L. Allen, *ibid.*, **86**, 5107 (1964).

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

[16] R. P. Bell and A. O. McDougall, *Trans. Faraday Soc.*, **56**, 1281 (1960).

three-halves power of the concentration of the peroxide. The kinetic dependence of the reaction on peroxydisulfate was determined in two ways—by varying the concentration of peroxide and observing the change in initial rate (see Figure 2) and from the linearity of integrated three-halves-order rate plots at ratios of peroxide–alcohol greater than 100. As this ratio falls below 100, the plots exhibit slight curvature during the initial portion of path B (see Figure 3). This initial deviation was observed by both Bartlett and Cotman[3] and Kolthoff, *et al.*,[2] but it was not further considered by them.

The curvature of integrated rate plots at the lowest alcohol concentrations, together with the decrease in the yields of formaldehyde under these conditions suggested that the product aldehyde was itself being oxidized and inhibiting the methanol oxidation. Indeed this was found to be the case, as is indicated by the data of Table II. The first five entries of Table II demonstrate the dependence of the rate constant obtained from integrated plots on methanol concentration; the middle three entries show the change in the initial rate constant as a function of alcohol concentration; the variation in rate constant as a function of the concentrations of both methanol and added formaldehyde are shown in the last six entries.

TABLE II

RATE CONSTANTS AS A FUNCTION OF METHANOL AND FORMALDEHYDE CONCENTRATIONS[a]

$[CH_3OH]_0$, M	$[CH_2(OH)_2]_0 \times 10^3$ M	$k_{3/2}$, $M^{-1/2}$ min^{-1}
1.5	0.0	1.62[b]
1.1	0.0	1.53[b]
0.78	0.0	1.41[b]
0.39	0.0	1.08[b]
0.20	0.0	0.97[b]
1.5	0.0	1.55[c]
0.79	0.0	1.49[c]
0.20	0.0	1.38[c]
1.6	7.7	1.27[b]
1.5	4.7	1.25[b]
1.5	16.6	1.06[b]
1.5	33.1	0.86[b]
0.80	7.7	1.00[b]
0.40	7.7	0.82[b]

[a] $[S_2O_8^{2-}]_0 \cong 8 \times 10^{-3}$ M, $T = 70°$. [b] Obtained from integrated rate plots; in the presence of added CH_2O some plots exhibited very soft sigmoidal shapes. [c] Obtained from initial rates.

The initial rate constants agree quite well with those calculated from integrated rate plots at 1.5 and 0.78 *M* alcohol. The value of the initial constant at the lowest methanol concentration is considerably larger than the corresponding value obtained from the integrated plots. The smaller value of the initial rate constant at 0.20 *M* alcohol may be due to some interference by formaldehyde, even under conditions where its concentration has been significantly reduced.

The data are consistent with a zero-order dependence of the rate on the concentration of methanol. The experimentally determined rate law for the B portion of the reaction for the concentration range explored is then

$$\frac{-d[S_2O_8^{2-}]}{dt} = k[S_2O_8^{2-}]^{3/2} \tag{3}$$

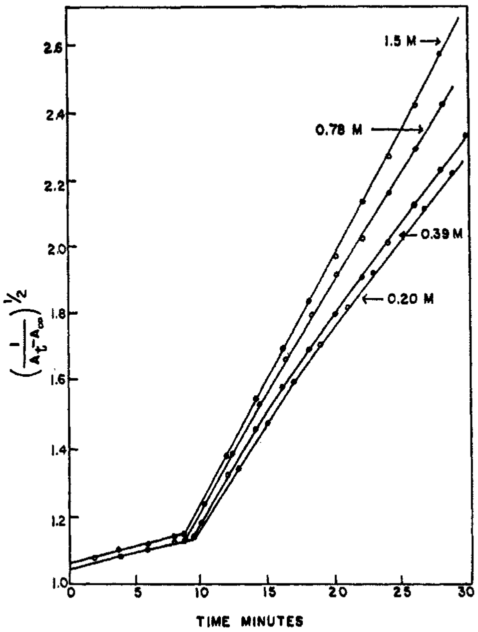

Figure 3.—Integrated rate plots for four methanol concentrations: $[S_2O_8^{2-}]_0 \cong 8 \times 10^{-3}$ M; $T = 70°$.

Deuterium Isotope Effect.—In order to gain further insight into the details of the path B mechanism, the effect of replacing the three α hydrogens of methanol with deuterium was investigated. The value of the initial three-halves-order rate constant at 70° and 0.80 *M* methanol-d_3 is 1.19 ± 0.03. This value in conjunction with that found for the protium compound at 0.79 *M* alcohol gives 1.25 ± 0.1 for the ratio k_H/k_D.

Activation Energy.—The Arrhenius activation parameters for path B were obtained in the interval 60–80°. Table III lists the values of the rate constant as a function of temperature. The values at the three highest temperatures were obtained from integrated rate plots. The preceding work has shown that at the concentrations of peroxydisulfate and methanol used in these runs, the aldehyde formed during the reaction does not affect the kinetics. However, at 60° the integrated plots exhibited an initial curvature analogous to that observed at lower alcohol concentrations and 70°. Thus, the 60° value was obtained from initial rates. A possible rationale concerning this observation will be considered in the discussion. The Arrhenius activation parameters are $A = 9.5 \times 10^{12}$ $M^{-1/2}$ sec^{-1} and $E_a = 23 \pm 1$ kcal mol^{-1}.

TABLE III

TEMPERATURE DEPENDENCE OF PATH A AND OF PATH B[a]

Temp, °C	$k_{3/2}$, $M^{-1/2}$ min^{-1}	R_A[b] $\times 10^4$ M min^{-1}	τ, min
60	0.57	0.42	29.5
70	1.62	1.17	7.1
75	2.58	2.25	4.1
80	3.82	3.7	2.6

[a] $[S_2O_8^{2-}]_0 \cong 8 \times 10^{-3}$ M, $[CH_3OH]_0 = 1.5$ M. [b] R_A = initial rate of path A.

Mechanism of Formaldehyde Inhibition.—Formaldehyde is itself capable of being oxidized by peroxydisulfate to yield formic acid.[17] The stoichiometry is given by eq 4. Equation 4 predicts that 3 mol of

$$S_2O_8^{2-} + CH_2(OH)_2 \longrightarrow HCOOH + 2H^+ + 2SO_4^{2-} \tag{4}$$

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[17] L. R. Subbaraman and M. Santappa, *Z. Phys. Chem.*, **48**, 172 (1966).

strong acid should be produced for each mole of peroxide consumed. It was found that for an initial peroxide concentration of 8.2×10^{-3} M and an equivalent concentration of formaldehyde, 86.5% of the theoretical amount of acid was formed; with a tenfold excess of formaldehyde the acid yield was 101%.

The foregoing data clearly indicate that aldehyde inhibition must involve the simultaneous oxidation of methanol and formaldehyde. If this is so, then at the lowest alcohol concentration an excess of titratable acid, formic acid, should be produced in addition to the 2 equiv of HSO_4^- predicted by eq 1. Table IV is a summary of the data obtained for the concentration of strong acid produced during the course of two experiments—one at a high alcohol concentration where the yield of formaldehyde has been found to be 100%, the other at a much lower concentration where only 82.5% of the total theoretical yield of aldehyde is produced. At 1.5 M alcohol only 2 mol of acid are produced, during and up to the completion of the reaction for each mole of peroxydisulfate consumed. These data also confirm the stoichiometry of the reaction with respect to acid production. At 0.10 M methanol, however, there is an increasing amount of acid produced with time over and above the stoichiometric quantity of eq 1. This "excess" acid is attributed to the oxidation of formaldehyde. Based on the 82.5% yield of H_2CO at 0.1 M alcohol, and assuming that the deficit of 17.5% is caused by the reaction of one-half of this deficit, or 8.75% of the initial peroxide with formaldehyde, the calculated excess concentration of acid at infinite time is 7.2×10^{-4} M. The excess found, 8.2×10^{-4} M, is in good agreement.

Table IV

Comparison of the Total Acid Produced with Peroxydisulfate Lost as the Reaction Proceeds[a]

$[CH_3OH]_0$, M	$[S_2O_8^{2-}]$ lost $\times 10^3$ M	$[H^+]/2$ gained $\times 10^3$ M	$\Delta \times 10^3$, M[b]
1.5	1.28	1.20	−0.08
1.5	4.25	4.28	+0.03
1.5	6.94	6.85	−0.09
1.5	8.52	8.48	−0.04
0.10	0.64	0.76	+0.12
0.10	2.37	2.66	+0.29
0.10	5.36	5.69	+0.33
0.10	8.19	8.60	+0.41

[a] $T = 70°$. [b] $\Delta = [H^+]/2$ gained $- [S_2O_8^{2-}]$ lost.

Effect of Additives.—The effect of a number of additives upon both paths of the reaction was investigated. These additives included Cu^{2+} and the disodium salt of ethylenediaminetetracetic acid (EDTA). The results of these experiments are listed in Table V. Also included therein are observations on the effects of solvent and purity of the potassium peroxydisulfate (as indicated by the number of recrystallizations from deionized water) employed in the kinetic runs.

The data indicate that under the conditions of our experiments up to 10^{-5} M Cu^{2+} can be tolerated without significant kinetic consequences to path B. Above 10^{-5} M, Cu^{2+} produces an increase in the rate of path B. Not only was a rate increase observed, but the kinetic dependence changed to first order in peroxydisulfate. This behavior contrasts sharply with the effect of Cu^{2+} on the path B oxidation of 2-propanol[7] where no effect of copper was found. A catalytic effect of Cu^{2+} was, however, also observed on path B by Gallopo for the system peroxydisulfate–ethanol.[13] A stoichiometric and kinetic study of the effect of Cu^{2+} on this system is reported in ref 13.

Table V

Effect of Additives, Solvent, and the Number of Recrystallizations of $K_2S_2O_8$[a]

$[CH_3OH]_0$, M	Additive	Conditions[b,c]	$R_A \times 10^4$,[f] M min^{-1}	τ, min	k_{obsd}
1.5	None	D, 1	1.17	7.1	1.62[d]
0.78	None	D, 1	1.29	8.1	1.42[d]
1.5	None	DI, 2	1.06	9.3	1.37[d]
0.78	N_2	D, 1	Not measurable	3.5	1.50[d]
1.5	1×10^{-5} EDTA	DI, 2	0.81[g]	11.3	1.37[d]
0.78	1×10^{-5} EDTA	D, 2	1.32	8.9	1.38[d]
1.5	1×10^{-5} EDTA	D, 2	1.17	8.9	1.44[d]
1.5	1×10^{-4} EDTA	D, 2	0.054	11.5	1.26[d]
1.5	1×10^{-5} Cu^{2+}	D, 2	1.27	8.0	1.72[d]
1.5	5×10^{-5} Cu^{2+}	D, 2	1.36	8.0	1.23[e]
1.5	1×10^{-4} Cu^{2+}	D, 2	1.42	7.5	1.84[e]

[a] $[S_2O_8^{2-}]_0 \cong 8 \times 10^{-3}$ M, $T = 70°$. [b] D = distilled water, DI = deionized water. [c] Number of recrystallizations of $K_2S_2O_8$ from DI water. [d] Obtained from integrated three-halves-order plots; units are $M^{-1/2}$ min^{-1}. [e] Obtained from integrated first-order plots; units are min^{-1}. [f] Obtained from traces of absorbance *vs.* time; R_A = initial rate of path A. [g] Value for one run; duplicate exhibited no change of absorbance with time.

EDTA was added to several reaction mixtures for which the solvent was either distilled or deionized water. In the presence of 10^{-5} M EDTA, the rate constants and the rate plots do not differ, within experimental error, from the behavior observed in the absence of EDTA. At 10^{-4} M EDTA the value of the rate constant is low, but the plots from which it was calculated exhibit initial curvature similar to that found in the case of aldehyde inhibition. Ball, *et al.*,[7] found that EDTA can react slowly with peroxydisulfate alone. The slight rate reduction may be due to a specific effect of EDTA itself, rather than to its ability to chelate trace metal ions.

Path A.—A study of path A was not the major purpose of this investigation, and, while the results do not permit firm mechanistic postulations, they are informative and agree generally with observations reported for 2-propanol[7] and ethanol.[13] The following data were obtained on solutions initially at equilibrium with air at room temperature. There was negligible space above solutions in the stoppered cuvettes and at the temperatures employed the rate of solution of additional oxygen is not thought to be important. Thus, τ may be considered an approximate measure of the original concentration of dissolved oxygen and $1/\tau$ is then proportional to the rate of oxygen consumption. The values of R_A and τ are probably of no greater accuracy than ±20%; deviations of this magnitude were found in duplicate runs.

The rate of path A appears to be independent of oxygen concentration. Although oxygen is necessary for path A to be observed, spectrophotometric traces are linear for the full length of A.[18] By varying the initial concentration of peroxydisulfate and methanol, path A was found to be independent of alcohol concentration, but not independent of peroxide. Log-log plots of the data of Table VI, for $[S_2O_8^{2-}]_A$ *vs.* R_A and τ have slopes of 0.81 and 0.86, respectively. Ar-

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(18) The traces are nonlinear for the first 1 or 2 min, during which time thermal equilibrium was established within the thermostated cell compartment following the mixing of reactants.

rhenius plots of R_A and τ data from Table III give apparent activation energies of 26 and 29 ± 2 kcal mol^{-1}. The larger value obtained from the τ data is as would be expected since temperature change would affect not only the rate of loss of oxygen but also its solubility.

The effects of additives upon path A are summarized in Table V. The only dramatic effect discernible is that of EDTA at 10^{-4} M in distilled water or 10^{-5} M EDTA in deionized water with twice recrystallized $K_2S_2O_8$. The comparatively small value of R_A at 10^{-4} M EDTA is difficult to interpret, as indicated in the discussion of the effects of additives on path B; it may be due to inhibition of the reaction by EDTA itself. The first-order rate constant calculated from R_A is 6.5×10^{-4} min^{-1} which is over two times slower than the rate constant for the thermal decomposition alone,[15] 1.45×10^{-3} min^{-1}. The effect of 10^{-5} M EDTA in deionized water with twice recrystallized $K_2S_2O_8$ may be real and due to reduced concentrations of trace metal ions. In a duplicate run under these conditions, however, there was no measurable change in absorbance during the entire course of A. With 10^{-5} M EDTA in distilled water there was no effect on either R_A or τ. These observations can be rationalized by assuming that path A is subject to trace metal catalysis; this is consistent with the reported effects of trace metals on the path A oxidation of 2-propanol[7] and ethanol.[13] When metal ion catalysis is eliminated, any inhibiting effect of EDTA itself would be more noticeable on a slower uncatalyzed path.[19]

TABLE VI
EFFECT OF VARIATION OF REACTANT CONCENTRATIONS ON PATH A AT 70°

$[CH_3OH]_0$, M	$[S_2O_8^{2-}]_A \times 10^3$ M	$R_A \times 10^4$ M min^{-1} [a]	τ, min
1.5	8.0	1.17	7.1
0.78	8.0	1.29	8.1
0.39	8.0	1.25	8.6
0.78	4.7	0.92	12.6
0.78	16.0	2.01	4.1
0.78	32.0	3.34	2.6

[a] R_A = initial rate of path A.

The lack of any appreciable effect of added Cu^{2+} in conjunction with the EDTA data indicate that the concentrations at which trace metal ions are able to catalyze path A must be extremely low and such catalysis must reach a limiting value at very small metal ion concentrations. Although Cu^{2+} is probably not the only catalytic ion present it has been found to be a very effective catalyst in peroxydisulfate oxidations.[7,13,14,20]

Oxidation of α-Phenylethanol.—Approximately 1 mol of acetophenone was formed for each mole of peroxydisulfate consumed. Based on the initial peroxide concentration under nitrogen and at 65–70° an 84% yield of the 2,4-dinitrophenylhydrazone of acetophenone was isolated. Spectrophotometrically determined yields ranged from 86 to 99%. All of the experiments listed in Table VII were conducted under nitrogen and pseudo-zero-order conditions at 10^{-4} M $K_2S_2O_8$ using deionized water. The data of Table VII are consistent with the following rate law for the production of acetophenone.

$$\frac{d[C_6H_5COCH_3]}{dt} = k[S_2O_8^{2-}][C_6H_5CHOHCH_3]^{1/2} \qquad (5)$$

TABLE VII
DEMONSTRATING THE DEPENDENCE OF THE THREE-HALVES-ORDER RATE CONSTANT ON REACTANT CONCENTRATIONS FOR THE OXIDATION OF α-PHENYLETHANOL[a]

$[S_2O_8^{2-}]_0 \times 10^4$ M	$[C_6H_5CHOHCH_3]_0 \times 10^3$ M	$k^{3/2}$ $M^{-1/2}$ min^{-1}
1.8	3.7	0.32
5.0	3.6	0.28
7.8	3.6	0.29
9.5	3.6	0.27
4.9	0.64	0.32
4.9	1.1	0.34
4.9	1.8	0.31
4.9	2.4	0.34
		Av 0.31 ± 0.02

[a] T = 55°, under nitrogen in deionized water.

Discussion

The oxidations reported herein clearly must proceed by a free-radical-chain mechanism initiated by the thermal decomposition of peroxydisulfate ion to two sulfate radical ions. Evidence supporting this statement is listed below.

(a) Peroxydisulfate ion has been shown to decompose in aqueous solution by a nonchain radical process.[15,21] It is well-known and widely used initiator of vinyl polymerizations.

(b) The oxidation of methanol is inhibited by oxygen and the oxidation of α-phenylethanol appears to be influenced by oxygen.[1] Oxygen inhibition of radical reactions involving organic compounds is a well-known phenomenon.

(c) The rates of these oxidations are a sensitive function of experimental conditions. The presence of oxygen, of trace metal ions, and of additives such as Cu^{2+} and formaldehyde have marked effects on rates. Such sensitivity is characteristic of radical reactions.

(d) The observed fractional dependence of rates on reactant concentrations is common for radical reactions.

(e) The deiodination of aryl iodides in methanolic sodium methoxide, which is postulated to occur *via* a free-radical mechanism, has been successfully initiated with $K_2S_2O_8$.[22]

(f) Allyl acetate and diphenylpicrylhydrazyl reduce the rate of loss of peroxydisulfate ion in the presence of alcohols to the rate of its decomposition in pure water.[2,13,21,23] Based on Kothoff and Miller's[15] values for the rate constant for the oxidation of water by $S_2O_8^{2-}$ the calculated chain lengths are, for methanol at 70° and 8×10^{-3} M $S_2O_8^{2-}$, 100, and, for α-phenylethanol at 55° 1.8×10^{-4} M $S_2O_8^{2-}$ and 3.6×10^{-3} M $C_6H_5CHOHCH_3$, 130.

Postulated Mechanisms.—The proposed mechanism for the path B oxidation of methanol for the case of negligibly small concentrations of $H_2C(OH)_2$, *i.e.*, during

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(19) Products of EDTA interference might absorb in the ultraviolet and cause the rate of change of absorbance to decrease to values less than those expected from the thermal decomposition of peroxydisulfate alone.

(20) Gallopo[13] has concluded that the following metal ions, present at a concentration of 10^{-5} M, as well as Cu(II), are probably capable of catalyzing the ethanol reaction: Ni(II), Fe(II), Cr(III), Hg(II), Sn(II), Sn(III), and Ti(II).

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

(22) J. F. Bunnett and Carl C. Wamser, *J. Amer. Chem. Soc.*, **89**, 6712 (1967).

(23) K. B. Wiberg, *ibid.*, **81**, 252 (1959).

the initial portion of path B or when the concentration of methanol is in 100-fold or greater excess over the initial concentration of $S_2O_8^{2-}$, is,

$$S_2O_8^{2-} \xrightarrow{k_1} 2\,SO_4\cdot^- \quad (6)$$

$$SO_4\cdot^- + CH_3OH \xrightarrow{k_2} \dot{C}H_2OH + H^+ + SO_4^{2-} \quad (7)$$

$$\dot{C}H_2OH + S_2O_8^{2-} \xrightarrow{k_3} CH_2O + H^+ + SO_4^{2-} + SO_4\cdot^- \quad (8)$$

$$\dot{C}H_2OH + \dot{C}H_2OH \xrightarrow{k_4} HOCH_2CH_2OH \quad (9)$$

$$CH_2O + H_2O \rightleftharpoons CH_2(OH)_2 \quad (2)$$

Assuming steady-state conditions for long chains these steps lead to the rate law

$$-\frac{d[S_2O_8^{2-}]}{dt} = k_3\left(\frac{k_1}{k_4}\right)^{1/2}[S_2O_8^{2-}]^{3/2}$$

This rate law agrees with our experimental results where $k = k_3(k_1/k_4)^{1/2}$.

The k_2 step probably involves abstraction of an α hydrogen from methanol and not the hydrogen bound to oxygen. Several pieces of evidence point to this conclusion: (a) esr spectra of radicals produced by hydrogen abstraction from alcohols by hydroxyl radicals have been shown to be consistent with removal of an α hydrogen;[24] (b) isotopic labeling experiments have provided evidence that attack by hydrogen atoms on hydroxylic hydrogens of alcohols does not readily occur;[25,26] (c) radical abstraction of α hydrogens should be approximately 9 kcal mol^{-1} more exothermic than hydrogen abstraction from the OH group of an alcohol.[27] The k_3 step explains the increased rate of loss of peroxydisulfate observed in the presence of alcohol compared with the rate of the water reaction. The chain termination reaction, k_4, is the only step consistent with the observed kinetics and proposed radical intermediates. The two organic radicals may either dimerize to ethylene glycol or disproportionate to methanol and formaldehyde. Photolysis experiments[28] on mixtures of water–hydrogen peroxide and the alcohols, methanol, ethanol, and 2-propanol, have shown that hydroxymethyl radicals prefer dimerization to disproportionation. Dimerization is also consistent with our kinetic deuterium isotope effect (*vide infra*).

An alternative mechanism involving HO· radicals is also reasonable. In our case such a mechanism would be kinetically indistinguishable from that proposed above. Recent work by Dogliotti and Hayon[29] on the flash photolysis of aqueous solutions of peroxydisulfate containing methanol, ethanol, and 2-propanol indicates that for the pH range 1–4.8 the sulfate radical ion reacts directly with alcohol by α-hydrogen abstraction.

The measured activation energy is also consistent with the proposed mechanism. The energy of activation, assuming all steps follow an Arrhenius temperature dependence, would be given by $E_a = E_3 + {}^1/_2(E_1 - E_4)$. E_1 has a value of approximately 33.5 kcal mol^{-1}.[15] E_4, the activation energy for the reaction of two radicals, should be very small;[30] for the purpose of this approximate calculation it is assumed that $E_4 = 0$. These values, together with the experimental value of E_a (23 kcal mol^{-1}), give $E_3 = 6.2$ kcal mol^{-1}; this is a reasonable value for the reaction of a radical and a molecule.[31]

The observed deuterium isotope effect provides further support for the proposed mechanism. The derived rate constant $k_3(k_1/k_4)^{1/2}$ does not contain k_2, the rate constant for abstraction of hydrogen by the sulfate radical ion. This leads to the prediction that the observed rate constant should be insensitive to deuterium substitution at the α carbon, *e.g.*, a primary isotope effect. The value of k_H/k_D of 1.25 ± 0.1 is of the magnitude expected for a secondary isotope effect on k_3 or an *inverse* secondary α-isotope effect on k_4.[32] Seltzer[33] has found that $k_H/k_D = 1.12$–1.15 per deuterium atom for radical-forming ractions. Since k_4 enters into the rate constant as $(1/k_4)^{1/2}$ the measured value of the rate constant for methanol-d_3 is predicted to be decreased by a factor of $(1/1.12^4)^{1/2}$ to $(1/1.15^4)^{1/2}$.[34-36] These ratios lead to values of 1.25–1.32 for k_H/k_D.

Mechanism of Formaldehyde Inhibition.—Formaldehyde inhibition is postulated to occur by steps analogous to those proposed above. In the inhibition

$$CH_2(OH)_2 + SO_4\cdot^- \xrightarrow{k_5} \dot{C}H(OH)_2 + SO_4^{2-} \quad (10)$$

$$\dot{C}H(OH)_2 + S_2O_8^{2-} \xrightarrow{k_6} HCOOH + H^+ + SO_4^{2-} + SO_4\cdot^- \quad (11)$$

$$\dot{C}H(OH)_2 + \dot{C}H_2OH \xrightarrow{k_7} \text{products} \quad (12)$$

mechanism k_5 and k_6 are added to the steps for path B oxidation of methanol and the k_4 step is replaced by k_7. Aldehyde inhibition is attributed to a more rapid reaction of the sulfate radical ion with aldehyde than with alcohol and a subsequent decrease in chain length as the termination step k_7 becomes operative.

When the steady-state approximation is applied to the sequence of steps 6–8 and 10–12, assuming long chains, eq 13 is obtained. According to eq 13 the

$$\frac{-d[S_2O_8^{2-}]}{dt} = \left(\frac{k_1k_3k_6}{k_7}\right)^{1/2}[S_2O_8^{2-}]^{3/2} \times \left[\left(\frac{k_2[CH_3OH]}{k_5[CH_2(OH)_2]}\right)^{1/2} + \left(\frac{k_5[CH_2(OH)_2]}{k_2[CH_3OH]}\right)^{1/2}\right] \quad (13)$$

initial three-halves-order rate constant for path B in the presence of added formaldehyde should be a function of the ratio of methanol to formaldehyde. A plot of $k_{3/2}([CH_3OH]_B/[CH_2(OH)_2]_B)$ *vs.* $[CH_3OH]_B/[CH_2(OH)_2]_B$ should be linear. The points of Figure 3 fit a straight line (correlation coefficient = 0.994) and are

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[24] M. C. R. Symons and M. G. Townsend, *J. Chem. Soc.*, 269 (1959).

[25] C. Lifshitz and G. Stein, *ibid.*, 3706 (1962), and references therein.

[26] J. H. Baxendale and G. Hughes, *Z. Phys. Chem.* (Frankfurt am Main), **14**, 306 (1958).

[27] J. W. Benson, *J. Chem. Educ.*, **42**, 502 (1965). The bond dissociation energies are CH_3O—H, 102 kcal mol^{-1}; $HOCH_2$—H, 93 kcal mol^{-1}.

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

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

[30] A. A. Frost and R. A. Pearson, "Kinetics and Mechanism," John Wiley & Sons, Inc., New York, N. Y., 1962, p 107.

[31] A. F. Trotman-Dickenson, "Free Radicals," John Wiley & Sons, Inc., New York, N. Y., 1959.

[32] S. Seltzer, private communication.

[33] A. Zavitsas and S. Seltzer, *J. Amer. Chem. Soc.*, **86**, 3836 (1964).

[34] According to Streitwieser's[35] treatment the isotope effect should be raised to the power of the number of deuterium atoms involved.

[35] A. Streitwieser, Jr., R. Jagow, R. Fahey, and S. Suzki, *J. Amer. Chem. Soc.*, **80**, 2326 (1958).

[36] This is not to say that radical coupling is expected to exhibit the same α-isotope effect as radical-forming reactions. Indeed, owing to the exothermicity of the former, k_H/k_D would be expected to be less than 12–15 % per deuterium.

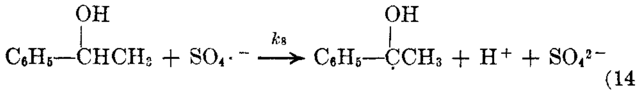
thus consistent with the proposed model. The ratio of the intercept to the slope of Figure 3 gives $k_5/k_2 = 11$.

The inequality $k_5 > k_2$ agrees with our suggested mechanism. Dogliotti[29] found that the reactivity of $SO_4\cdot^-$ toward alcohols increases in the order methanol, ethanol, 2-propanol—the order of expected stability of the incipient radical. Since the substitution of one OH group increases the stability of the radical produced by α-hydrogen abstraction from methanol over a methane radical, substitution of hydrogen by two hydroxyl groups should further increase the stability of the formaldehyde radical.[38]

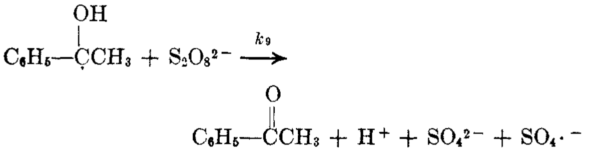
Subbaraman[17] reports that the peroxydisulfate oxidation of formaldehyde is only about ten times faster than the water oxidation rate. He proposes a radical chain mechanism involving steps 10 and 11.[40] Thus it appears that although k_5 is greater than k_2, k_6 must be much smaller than k_3; the radical $\cdot CH(OH)_2$ would then be able to reach a relatively high steady-state concentration and decrease the chain length in our case by termination with the radical $\cdot CH_2OH$.[41]

Path A.—We attribute the lower rate of loss of peroxydisulfate in path A to a reaction between the reducing radical $\cdot CH_2OH$ and molecular oxygen. Oxygen inhibition probably occurs by a mechanism similar to that proposed by Ball, *et al.*,[7] and Gallopo[13] for the path A oxidations of 2-propanol and ethanol, respectively. There are, however, subtle differences in the behavior of the three alcohols. These differences are reflected in the effects of additives such as Cu^{2+} and EDTA. The reasons for this are not presently clear.

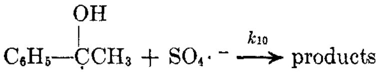
α-Phenylethanol.—We propose the following chain mechanism, initiated by eq 6 to account for the observed kinetics of oxidation of α-phenylethanol.



$$C_6H_5\text{—}\overset{\text{OH}}{\overset{|}{C}}HCH_3 + SO_4\cdot^- \xrightarrow{k_8} C_6H_5\text{—}\overset{\text{OH}}{\overset{|}{\underset{\cdot}{C}}}CH_3 + H^+ + SO_4^{2-} \tag{14}$$



$$C_6H_5\text{—}\overset{\text{OH}}{\overset{|}{\underset{\cdot}{C}}}CH_3 + S_2O_8^{2-} \xrightarrow{k_9} C_6H_5\text{—}\overset{\text{O}}{\overset{\|}{C}}CH_3 + H^+ + SO_4^{2-} + SO_4\cdot^- \tag{15}$$



$$C_6H_5\text{—}\overset{\text{OH}}{\overset{|}{\underset{\cdot}{C}}}CH_3 + SO_4\cdot^- \xrightarrow{k_{10}} \text{products} \tag{16}$$

For long chains these steps lead to the rate law

$$\frac{d[C_6H_5COCH_3]}{dt} = \left(\frac{k_1k_8k_9}{k_{10}}\right)^{1/2}[S_2O_8^{2-}][C_6H_5CHOHCH_3]^{1/2} \tag{17}$$

Equation 17 is of the same form as the rate law found experimentally.

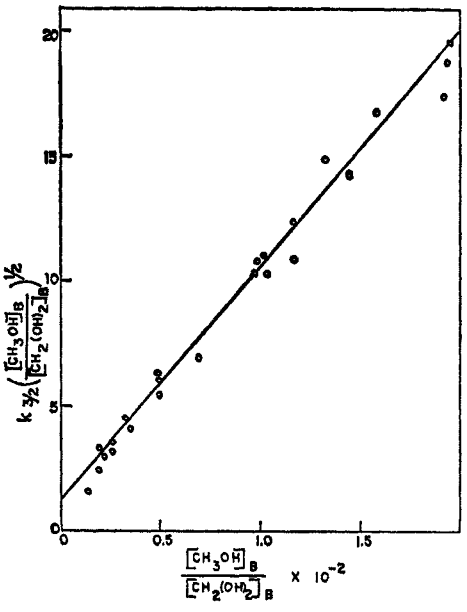


Figure 4.—Fit of experimental data to eq 13: $[S_2O_8^{2-}] \cong 8 \times 10^{-3}$ *M*, $T = 70°$; $[CH_2(OH)_2]_B$ = added $CH_2(OH)_2$ plus $[CH_2(OH)_2]$ theoretically formed during path A.[37]

General Conclusions.—From our work and from the reported rate laws and proposed oxidation mechanisms of alcohols by peroxydisulfate[4-7,13] a general pattern has emerged. Primary and secondary alcohols are, in the absence of oxygen, oxidized by similar mechanisms. The only difference between the two classes of alcohol is that the rate laws for primary alcohols require a chain termination between two organic radicals whereas secondary alcohols must chain terminate by reaction of an organic radical and the sulfate radical ion if the proposed mechanisms are to yield rate laws conforming to experimental results.[42] It has been found that radicals which can exhibit opposite polar effects in chain propagation steps usually favor cross-termination.[43] In radical termination steps the activation energy barrier may be reduced by polar contributions from a donor and an acceptor radical,[43] even though the activation barrier for all such reactions is expected to be small.[30] Gallopo[13] reports a 150-fold rate reduction in going from ethanol to 2,2,2-trifluoroethanol; this is good evidence that electronic effects are indeed important in peroxydisulfate–alcohol reactions.[44] The radicals originating from secondary alcohols would be expected to have electron donor qualities relative to the sulfate radical ion; such qualities should favor cross-termination. Primary alcohol radicals, according to this argument, would then be predicted to self-terminate.[45]

Registry No.—Methanol, 67-56-1; α-phenylethanol, 98-85-1; peroxydisulfate ion, 15092-81-6.

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[37] The yield data of Table I and the experiments with formaldehyde show that for the concentrations employed the majority of $S_2O_8^{2-}$ is lost by reaction with methanol.

[38] The dissociation energies are CH_3—H, 101^{39} kcal mol^{-1}; $HOCH_2$—H, 93^{27} kcal mol^{-1}.

[39] T. L. Cottrel, "The Strengths of Chemical Bonds," Butterworth and Co. Ltd., London, 1958, p 177.

[40] The initiation step proposed by Subbaraman is doubtful since it involves a bimolecular reaction between $CH_2(OH)_2$ and $S_2O_8^{2-}$, see E. J. Behrman and J. E. McIsaac in "Mechanisms of Reactions of Sulfur Compounds," N. Kharasch, Ed., Vol. 2, 1968, for a more complete discussion.

[41] Assuming similar preexponential Arrhenius factors for steps 10 and 7, the ratio k_5/k_2 corresponds to an apparent difference of 1.6 kcal mol^{-1} in E_a. The nonlinear rate plots obtained at 60° (*vide ante*) can be rationalized; at the lowest temperature $CH_2(OH)_2$ would be expected to react with $SO_4\cdot^-$ more rapidly, relative to CH_3OH, than it does at 70°. This argument is supported by the general decrease in the yields of formaldehyde with decreasing temperature; see Table I.

[42] The only exception is cyclohexanol[6] for which participation by the hydroxyl radical must be invoked.[40]

[43] C. Walling, "Free Radicals in Solution," John Wiley & Sons, Inc., New York, N. Y., 1957, p 146.

[44] D. D. Tanner and S. A. A. Osman, *J. Amer. Chem. Soc.*, **90**, 6572 (1968).

[45] There is no evidence in the literature, with the exception of that cited,[42] for these reactions requiring other possible termination steps, *e.g.*, those between two $SO_4\cdot^-$ radicals or others involving HO·radicals.