lated position of pinitol is assigned the number 3, and the sulfonylated position the number 4, while in other cases the opposite is true. Similar numbering shifts occur with the *allo*-inositol derivatives, accompanied by a change in the designation of configurational series (D or L). These unfortunate variations result from the necessity of choosing between the two equivalent numberings inherent in the stereochemistry of each of the parent inositols. The choice is made by the principle of "lowest number to the substituent first in alphabetical order," which seems the least undesirable of the alternatives available for dealing with this situation. Confusion is best avoided by constant reference to formulas **2** and **5.**

(37) S. J. Angyal and T. S. Stewart, *Aust. J. Chem.*, **20,** 2117 (1967).

(38) J. W. Arnold, *Ind. Eng. Chem., Anal. Ed.*, **17,** 215 (1945). We did not find it necessary to remove the bulk of the precipitated silver azide by filtration before completing the titration.

(39) F. Loewus and R. H. Shah, *Methods Carbohyd. Chem.*, **6,** 14 (1972).

(40) H. H. Hodgson and W. H. H. Norris, *J. Chem. Soc.*, 762 (1949).

(41) M. T. Reagan and A. Nickon, *J. Amer. Chem. Soc.*, **90,** 4096 (1968).

Kinetics and Mechanism of Alkyl Ether Oxidation by Peroxydisulfate Ion

Ruggero Curci,[1a] George Delano,[1b] Fulvio DiFuria,[1a] John O. Edwards,[1a] and Andrew R. Gallopo*[1b]

Departments of Chemistry, Brown University, Providence, Rhode Island 02912, and Montclair State College, Upper Montclair, New Jersey 07043

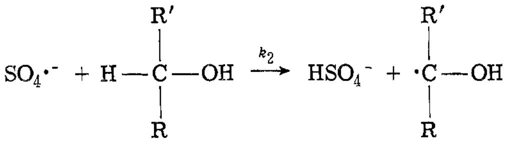
Received June 20, 1974

The oxidation of three ethers (*p*-dioxane, tetrahydrofuran, and diethyl ether) by peroxydisulfate ion in aqueous solution has been investigated. The rate law is $-d[S_2O_8^{2-}]/dt = k_{obsd}[S_2O_8^{2-}]^{3/2}$ with the value of k_{obsd} depending on the nature of the ether. The rate law, rate constants, influences of oxygen gas and cupric ion, and activation energies indicate a radical chain mechanism closely similar to that known for the oxidation of primary alcohols by peroxydisulfate. Chain lengths have been evaluated, and the influences of aldehydes on rates were investigated. Some of the products of ether oxidation (vinyl ethers and their oligomers) are different from those found in alcohol oxidation. Similarities in and differences between the reactions for the two classes of organic oxygen compounds are discussed.

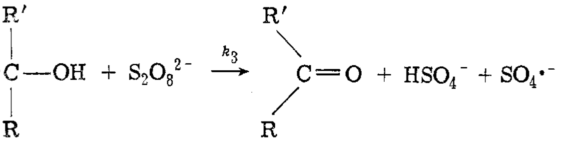
The general features of the peroxydisulfate oxidation of primary and secondary alcohols have been elucidated in the work of this group[2,3] and in other laboratories.[4] Evidence was reported for a free-radical chain mechanism which involves as initiation step the unimolecular homolytic dissociation of $S_2O_8^{2-}$

$$S_2O_8^{2-} \xrightarrow[\Delta]{k_1} 2SO_4^{\cdot -} \qquad (1)$$

and the following as propagation steps

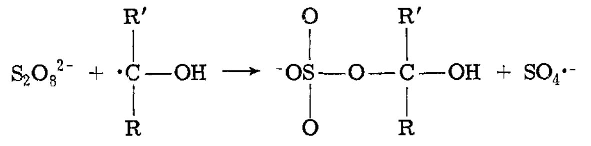


$$SO_4^{\cdot -} + H-\underset{R}{\overset{R'}{C}}-OH \xrightarrow{k_2} HSO_4^- + \cdot\underset{R}{\overset{R'}{C}}-OH \qquad (2)$$



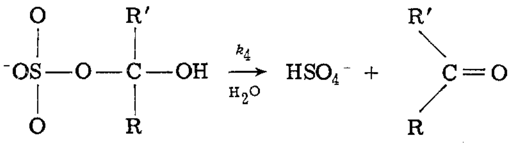
$$\cdot\underset{R}{\overset{R'}{C}}-OH + S_2O_8^{2-} \xrightarrow{k_3} (R')(R)C{=}O + HSO_4^- + SO_4^{\cdot -} \qquad (3)$$

where R′ = R′ = H; R = H and R′ = CH_3; and R = R′ = CH_3. Nevertheless, the exact nature of the third step of the chain was not understood because two reasonable transition state configurations can be visualized. Both of these two pathways seem consistent with the formation of the observed products. One pathway involves the formation of an hemiacetal-like intermediate by carbon attack on peroxide oxygen



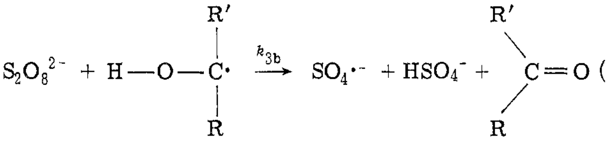
$$S_2O_8^{2-} + \cdot\underset{R}{\overset{R'}{C}}-OH \longrightarrow {}^-O\underset{O}{\overset{O}{S}}-O-\underset{R}{\overset{R'}{C}}-OH + SO_4^{\cdot -} \qquad (3a)$$

and its subsequent breakdown.



$${}^-O\underset{O}{\overset{O}{S}}-O-\underset{R}{\overset{R'}{C}}-OH \xrightarrow[H_2O]{k_4} HSO_4^- + (R')(R)C{=}O \qquad (4)$$

The other mechanism involves the direct breaking of the oxygen–hydrogen bond (*i.e.*, hydrogen atom transfer) during attack on peroxide oxygen.



$$S_2O_8^{2-} + H-O-\underset{R}{\overset{R'}{C}}\cdot \xrightarrow{k_{3b}} SO_4^{\cdot -} + HSO_4^- + (R')(R)C{=}O \qquad (3b)$$

The termination step for ethanol involves two organic radicals (reacting by either disproportionation or dimerization).

$$2CH_3\dot{C}HOH \longrightarrow \text{products} \qquad (5)$$

It was deemed worthwhile to carry out a kinetic study of the peroxydisulfate oxidations of ethers. Assuming that the alcohol and ether oxidations proceed by analogous mechanisms, in the case of the ethers the latter pathway (eq 3b) proposed for the third step is clearly impossible. A comparison of the relative rates for alcohols and ethers could then lead to better understanding of the behavior of the reaction of the α-oxyalkyl radical and the peroxydisulfate anion.

Moreover, in the general field of peroxide oxidation of the ethers, very interesting characteristics have been found.[5] A free-radical chain mechanism for the ether-induced decomposition of benzoyl peroxide has been demonstrated. The propagation steps are believed to be the formation of an α-oxyalkyl radical from the ether and the reaction of this radical with the peroxide.

The production of dioxanyl radicals by reaction of the sulfate radical ion $SO_4\cdot^-$ (from peroxydisulfate ion) with dioxane and the subsequent dioxanylation of some heteroaromatic bases have been recently reported by Minisci and coworkers,[6] and a kinetic study of the peroxydisulfate oxidation in the presence of silver ion has been carried out by Mishra and Ghosh.[7]

On the other hand, the kinetic behavior of the reaction of ethers and peroxydisulfate alone has never been studied extensively. This investigation was undertaken in order to elucidate the general features of the reaction mechanism as well as to compare the results with those obtained for the peroxydisulfate oxidation of alcohols.

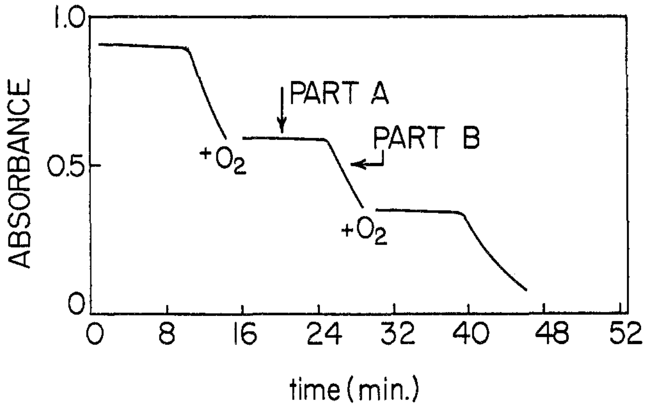


Figure 1. A schematic line drawing showing the behavior of absorbance (due to peroxydisulfate ion) as a function of time. Part A (reaction under oxygen inhibition) is followed by part B (when oxygen is consumed); also part A can be reestablished if the spectrophotometer cell is opened and oxygen is admitted.

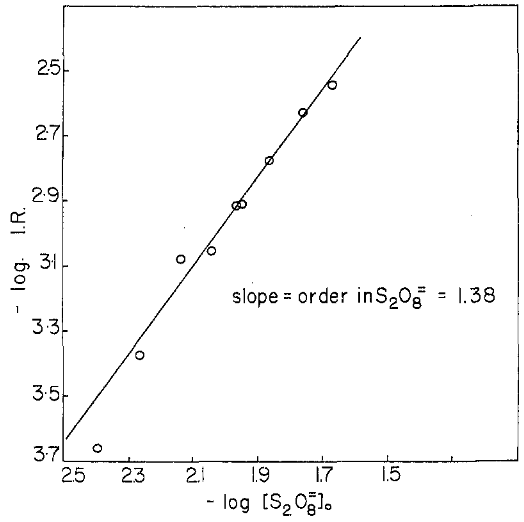


Figure 2. A plot of log (initial rate) against log $[S_2O_8^{2-}]_0$ at 70° to obtain the kinetic order in peroxydisulfate ion. A similar plot for the same reaction (dioxane oxidation) but at 60° gave a slope of 1.58.

Results

General. When the oxidation of an ether was started in a stoppered cell or in a vessel under a nitrogen atmosphere, a small increase in the absorbance was usually observed at the beginning. This increase was paralleled by a small increase in the amount of peroxide (as shown by iodometric analysis). The absorbance increase was, therefore, ascribed to a minor temperature effect plus peroxide being formed by the induced reduction of oxygen. When the solutions were not kept under nitrogen, both effects were enhanced and dissolved oxygen is clearly implicated. Further, the runs were followed by absorbance at 230 mμ, which is a wavelength where all peroxides absorb.[8] This effect due to dissolved oxygen was obvious for dioxane and tetrahydrofuran but small for diethyl ether. The peroxide concentration quickly reached a maximum and little further variation of the concentration was observed for several minutes. Then, a relatively rapid loss of peroxydisulfate begins and the rate of this reaction is considerably larger than the thermal decomposition of peroxydisulfate ion alone at the same temperature.

The rapid reaction is immediately quenched if a small amount of air is introduced in the reacting system (see Figure 1). The effect of the addition of allyl acetate in low concentration to the reagents was studied in the case of dioxane oxidation and the results indicated that the reaction rate (as evidenced by peroxydisulfate concentration change) is lowered to that observed in the thermal decomposition of peroxydisulfate ion alone. In general characteristics, this behavior is similar to that observed in the peroxydisulfate oxidation of the alcohols.

Using the same nomenclature as employed earlier[2,3] we designate the first portion of the reaction as path A and its length as τ, and the second fast portion as path B. As in the oxidation of the alcohols, path A was evidenced by a very slow loss of peroxydisulfate; the observed increase of the total peroxide concentration in the ether oxidations (also reported in the benzoyl peroxide oxidations of organic compounds[8]) is probably due to the formation, in the reaction medium, of relatively stable peroxides derived from the ethers by reaction of the dissolved oxygen with organic radicals.

Product Compositions. For all three ethers, olefins, aldehydes, and oligomeric products were observed. The vinyl compounds and their oligomers were detected by mass spectrometry. A number of peaks, some of which are parent peaks for the olefins and others of which appear as parent peaks in the molecular weight range from 200 to 300, were observed. The latter set is due to oligomers. The amount of vinyl ether decreased slowly on standing with simultaneous increase in amounts of oligomer. Acids (HSO_4^- in our case) are known to bring about slow polymerization of vinyl ethers.

The amounts of aldehyde as indicated by the characteristic carbonyl absorption were very small for dioxane and tetrahydrofuran. In fact, there was too little change in absorption near 280 mμ to allow quantitative evaluation. On the other hand, acetaldehyde seems to be the predominant product in the ethyl ether oxidation. It was isolated as the 2,4-dinitrophenylhydrazone. In the reaction mixture, quantitative evaluation of acetaldehyde was possible in the ultraviolet spectra. Some results are given in Table I. The yields run from 64 to 86%. As expected from the alcohol oxidations, the yield of carbonyl compound was greater when the amount of ether increased. It appears that the yield of carbonyl product also increased with temperature.

Table I
Yield of Acetaldehyde in the Peroxydisulfate Oxidation of Ethyl Ether

$[S_2O_8^{2-}]_0 \times 10^3$, M	$[Et_2O]_0$, M	$[CH_3CHO] \times 10^3$, M	Temp, °C	Yield, %
13.60	0.132	9.5	60	69
6.80	0.132	4.5	60	67
6.80	0.264	5.0	60	73
6.80	0.066	4.3	60	64
6.80	0.132	4.6	71	67
6.80	0.132	5.8	81	86

It is worthy of note here that carbon–carbon double bonds are also formed in the peroxydisulfate oxidation of tertiary amines.[9]

Rate Law. The kinetic dependence of the path B reaction on peroxydisulfate concentration was determined by varying the amount of peroxide, at fixed ether concentration, and observing the changes in initial rate (IR) of path B. Independent sets of data are given in Table II, which has two parts showing the results obtained in our two laboratories. Also presented are two figures showing some of the

Table II
Dependence of Rates on Peroxydisulfate Concentration

Ether	$[S_2O_8^{2-}]_0 \times 10^3$, M	IR^d × 10^5, M sec^{-1}	$k_{3/2} \times 10^2$, $M^{-1/2}$ sec^{-1}
Ethyl ether[a]	13.6	5.01	4.5
	6.8	1.80	4.9
	2.7	0.20	4.4
	1.4	0.15	4.2
Tetrahydrofuran[b]	33.1	6.19	1.0
	26.5	3.74	1.0
	13.2	1.46	1.1
	6.6	0.41	1.0
	2.6	0.22	
Dioxane[c]	33.0	2.07	0.44
	22.6	1.47	0.48
	16.9	1.03	0.60
	11.8	0.60	
	8.4	0.39	0.63
	6.5	0.25	0.66
	4.2	0.11	
	3.4	0.08	
Dioxane[e]	20.8	4.80	1.60
	17.2	3.88	1.72
	14.0	2.82	1.70
	10.8	2.08	1.86
	9.0	1.48	1.73
	7.2	1.39	2.27
	5.4	0.70	1.79
	4.0	0.37	1.49

[a] [Ethyl ether]$_0$ = 0.132 M, temperature 60°. [b] [Tetrahydrofuran]$_0$ = 0.57 M, temperature 60°. [c] [Dioxane]$_0$ = 0.68 M, temperature 60°. [d] IR = initial rate of loss of $S_2O_8^{2-}$. [e] Temperature 70°, [dioxane]$_0$ = 0.74 M.

Table III
Dependence of Rate on Ether Concentration

Ether	[Ether]$_0$, M	IR^d × 10^5, M sec^{-1}	$k_{3/2} \times 10^2$, $M^{-1/2}$ sec^{-1}
Ethyl ether[a]	0.066	1.66	4.6
	0.132	1.80	4.9
	0.264	1.92	4.7
Tetrahydrofuran[b]	0.24	2.60	1.5
	0.36	1.95	1.3
	0.48	2.60	1.5
	0.96	3.26	2.1
	1.20	3.10	1.7
	1.44	3.58	2.1
	1.80	3.42	1.7
	2.40	4.23	1.9
Dioxane[c]	0.34	1.12	0.57
	0.54	1.20	0.57
	0.69	1.03	0.60
	0.92	0.87	
Dioxane[e]	0.37	1.62	2.35
	0.74	1.87	2.72
	1.11	1.53	2.24
	1.48	1.38	2.02
	1.85	1.53	2.24
	2.22	1.53	2.24
	2.59	1.30	1.90

[a] $[S_2O_8^{2-}]_0$ = 6.80 × 10^{-3} M, temperature 60°. [b] $[S_2O_8^{2-}]_0$ = 1.74 × 10^{-2} M, temperature 60°. [c] $[S_2O_8^{2-}]_0$ = 1.70 × 10^{-2} M, temperature 60°. [d] IR = initial rate of loss of $S_2O_8^{2-}$. [e] Temperature 70°, $[S_2O_8^{2-}]_0$ = 7.8 × 10^{-3} M.

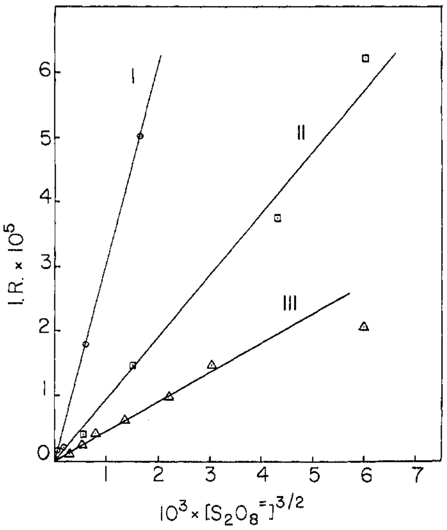


Figure 3. Plots of initial rate as a function of the three-halves power of $[S_2O_8^{2-}]_0$ to show the linear dependence (thus three-halves order) and zero intercept (thus no competing path). Data for three ethers (I, ethyl ether; II, tetrahydrofuran; and III, dioxane) at 60°.

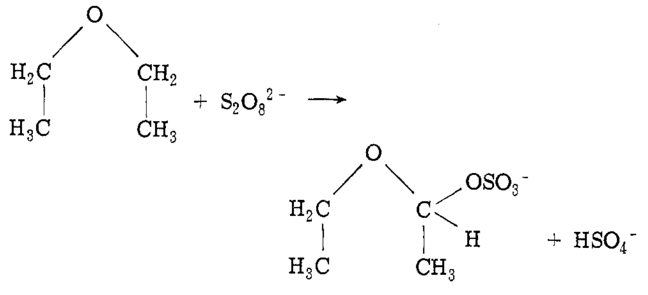
order dependence data. These results plus the linearity of integrated three-halves-order plots indicate that the exponent on the peroxide concentration in the rate law is three-halves.

By varying the initial concentration of the ethers (Table III), a zero-order dependence (*i.e.*, independence) of the rate on ether was found. Therefore, the experimentally determined rate law for the B portion of the reaction, for the concentration ranges explored, is

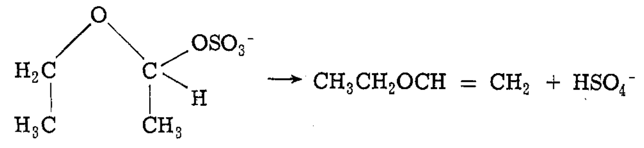
$$\frac{-d[S_2O_8^{2-}]}{dt} = k[S_2O_8^{2-}]^{3/2}$$

Activation Energies. In Table IV are listed the values of the rate constants as a function of temperature for the dioxane and ethyl ether oxidations. The activation energies are 24 and 17 kcal mol^{-1} for dioxane and ethyl ether, respectively.

Effects of the Products. The oxidation of alcohols had a simple stoichiometry with carbonyl compounds being the predominant organic product. It was expected that the ether oxidation would go to acetal-like products, which



would then hydrolyze with production of carbonyl compound. In fact, it turned out that significant quantities of olefinic products are formed. These presumably are derived by elimination of HSO_4^- from the acetal. In the case



of ethyl ether above, vinyl ethyl ether is therefore the specific ether predicted and has been found to be one product; acetaldehyde has also been isolated and identified (see above). In view of these results, some influence of product on rate of ether oxidation is expected. For the three ethers, the values of $k_{3/2}$ obtained by extrapolation from the initial rates (Table V) are smaller than the $k_{3/2}$ values obtained from the three-halves-order integrated plots. This behavior can be rationalized as a catalytic effect of the product of the reaction. By way of comparison, in the ethanol oxidation the product acetaldehyde was found to act as an inhibitor of the oxidation; the aldehyde can be easily oxidized and inhibits the alcohol oxidation by changing the nature of the termination step.[3]

Table IV
Temperature Dependence of Path B

Ether	Temp, °C	$k_{3/2} \times 10^2$, $M^{-1/2}$ sec^{-1}
Ethyl ether[a]	60.0	4.9[c]
	71.0	15.6[c]
	81.0	29.4[c]
Dioxane[b]	60.0	0.56[c]
	70.0	2.1[c,d]
	80.5	4.7[c]

[a] $[S_2O_8^{2-}]_0 = 6.80 \times 10^{-3}$ *M*, [ethyl ether]$_0$ = 0.132. [b] $[S_2O_8^{2-}]_0 = 5.5 \times 10^{-3}$ *M*, [dioxane]$_0$ = 0.68 *M*. [c] Average of three independent determinations. [d] This value is from B. U.; the value from M. S. C. obtained independently is 2.2.

Table V
Comparison of the $k_{3/2}$ Values Obtained by Extrapolation from the Initial Rates and the $k_{3/2}$ Values Obtained from the Integrated Plots[a,b]

Ether	$k_{3/2}$ (extr) × 10^2	$k_{3/2}$ (int) × 10^2
Ethyl ether	3.2	4.6
Tetrahydrofuran	0.9	1.6
Dioxane	0.47	0.56

[a] The $k_{3/2}$ values are averages taken from kinetic runs under conditions and with concentrations similar to those in Tables II and III. The $k_{3/2}$ (extr) are values obtained from initial slopes and the $k_{3/2}$ (int) values come from slopes of integrated plots. [b] Data for 60°, and the units of $k_{3/2}$ are $M^{-1/2}$ sec^{-1}.

Some experiments were therefore performed in order to evaluate the effect of aldehydes on dioxane oxidation. Small changes in rate were observed but no serious inhibiting effect of glyoxal on the reaction and no hydroxyacetaldehyde were observed. In the case of acetaldehyde, there is an enhancement of the rate of loss of peroxydisulfate. At higher concentrations of acetaldehyde, the catalytic effect ceases and the incursion of an inhibitory effect is observed. Further details of these results may be obtained on request; however, the conclusions we arrive at are not changed due to these minor influences of aldehydes.

Influence of Copper. It was found in the alcohol oxidations that cupric ion has an effect on rate and mechanism.[2,3] We deemed it important to see if this metal ion would influence the ether oxidation in a similar manner.

The effect of copper was of less importance for dioxane than was found for ethanol,[3c] but the difference was not great. The order in peroxydisulfate dropped from three-halves for the uncatalyzed path to one; the data are presented in Table VI and these form an order slope of 1.04. The order in copper was about 0.4 in the range of $[Cu^{2+}]$ from 2×10^{-5} to 2×10^{-4} *M*, and some results are given in Table VII. The rate depended slightly on concentration of dioxane at low concentrations, but at concentrations near 1

M there was no further change; we feel that the changes are so small that they cannot be considered evidence for a true kinetic order. Thus the rate law for the copper-catalyzed path is considered to be

$$\text{rate} = k[S_2O_8{}^{2-}][Cu^{2+}]^{1/2}$$

This is the same rate law that was found for the copper-catalyzed oxidation of ethanol.[3c]

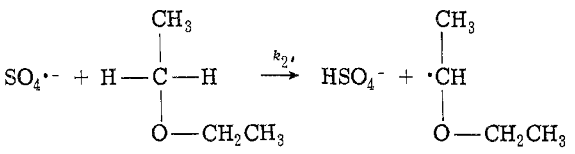
Discussion and Conclusions

The ether oxidation reactions clearly proceed by a free-radical chain mechanism. The evidence supporting this conclusion is as follows: (a) inhibition by oxygen (which is known to react rapidly with organic radicals), (b) inhibition by allyl acetate (known to react rapidly with sulfate radical ions), (c) sensitivity of rates to low concentrations of additives such as Cu^{2+} and aldehydes, (d) fractional orders (*i.e.*, nonintegral dependence of rates on reagent concentrations), and (e) activation energy values between $E_a'/2$ and E_a' (where E_a' is the activation energy, 33.5 kcal mol^{-1}, for the k_1 step).

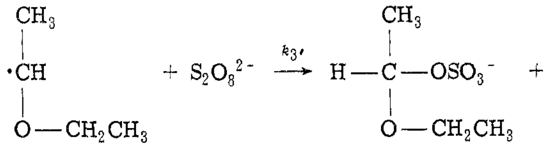
All of these results were also seen in the alcohol oxidations, and there are some quantitative similarities as well. The rate law for ethyl ether oxidation is the same as that observed for ethyl alcohol oxidation. Also the rate constants and activation energies are very similar for oxidation of these two structurally related compounds (see ref 3c).

The products in the ether oxidation are dramatically different from those obtained in the oxidation of alcohols wherein the yields of carbonyl compounds were nearly quantitative when $[CH_3CH_2OH] \gg [S_2O_8{}^{2-}]$. Both the kinetic similarities and the stoichiometric differences must be explained in any suggested mechanism. Therefore, using ethyl ether as example, we propose the following mechanism.

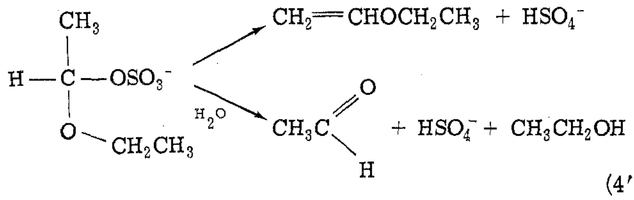
$$S_2O_8{}^{2-} \xrightarrow{k_1} 2SO_4{}^{\cdot -} \quad (1)$$



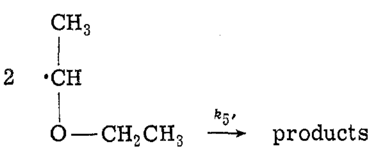
$$SO_4{}^{\cdot -} + H\text{—}C(CH_3)(OCH_2CH_3)\text{—}H \xrightarrow{k_{2'}} HSO_4{}^- + {\cdot}CH(CH_3)OCH_2CH_3 \quad (2')$$



$${\cdot}CH(CH_3)OCH_2CH_3 + S_2O_8{}^{2-} \xrightarrow{k_{3'}} H\text{—}C(CH_3)(OCH_2CH_3)\text{—}OSO_3{}^- + SO_4{}^{\cdot -} \quad (3'a)$$



$$H\text{—}C(CH_3)(OCH_2CH_3)\text{—}OSO_3{}^- \rightarrow CH_2{=}CHOCH_2CH_3 + HSO_4{}^-$$
$$H\text{—}C(CH_3)(OCH_2CH_3)\text{—}OSO_3{}^- \xrightarrow{H_2O} CH_3CHO + HSO_4{}^- + CH_3CH_2OH \quad (4')$$



$$2\,{\cdot}CH(CH_3)OCH_2CH_3 \xrightarrow{k_{5'}} \text{products} \quad (5')$$

Steps 2′, 3′a, and 5′ are analogous to steps 2, 3a, and 5 of the alcohol oxidation. Step 1 is, of course, identical since it does not involve any organic particle. Step 4′ is given as two separate paths for breakdown of the acetal-like intermediate; for step 4, only one path is given because only aldehyde is observed (as a primary product) in alcohol oxidation.

Table VI
Determination of Order in Peroxydisulfate Concentration[a]

$[S_2O_8{}^{2-}] \times 10^{-2}$, *M*	Nm[b]	IR[c] × 10^{-3}
2.72	247	3.92
1.97	242	3.25
1.60	239	2.27
1.00	232	1.50
0.69	227	1.05
0.41	221	0.62

[a] [Dioxane] = 0.72 *M*, [Cu(II)] = 1.0×10^{-4} *M*, temperature 60°. [b] Wavelength of analysis, chosen to give full scale deflection. [c] Initial rate in units of mol l.$^{-1}$ min^{-1}.

Table VII
Determination of Order in Copper(II) Concentration[a]

[Cu(II)], *M*	IR[b]	[Cu(II)], *M*	IR[b]
2×10^{-4}	1.26×10^{-3}	6×10^{-5}	1.08×10^{-3}
1×10^{-4}	1.19×10^{-3}	4×10^{-5}	0.90×10^{-3}
8×10^{-5}	1.19×10^{-3}	2×10^{-5}	0.67×10^{-3}

[a] $[S_2O_8{}^{2-}] = 1.2 \times 10^{-2}$ *M*, [dioxane] = 0.36 *M*, temperature, 60°. [b] Initial rate in units of mol l.$^{-1}$ min^{-1}.

Assuming steady-state conditions, the mechanism leads to the derived rate law

$$\frac{-d[S_2O_8{}^{2-}]}{dt} = k_{3'a}\left(\frac{k_1}{k_{5'}}\right)^{1/2}[S_2O_8{}^{2-}]^{3/2}$$

in agreement with the experimental law. Thus $k_{3/2} = k_{3'a}(k_1/k_{5'})^{1/2}$.

At 60° with $[S_2O_8{}^{2-}] \simeq 0.02$ *M* and [ether] $\simeq 0.4$ *M*, the estimated chain lengths are as follows: for ethyl ether, 1000; for dioxane, 100; and for tetrahydrofuran, 250. These can be compared with the value of 600 for ethyl alcohol at 70° and roughly similar concentrations. The termination step is the reaction of two α-oxyalkyl radicals, but the kinetics are consistent with either a dimerization or a disproportionation in this step.

The presence of both acetaldehyde and vinyl ethyl ether in the oxidation of ethyl ether suggests that the two different products are formed by breakdown of a common intermediate: the pseudoacetal formed in step 3′. This is reasonable if one considers that the reaction of an α-oxyalkyl radical and the peroxydisulfate ion leads, in the case of the alcohols, to the formation of a pseudohemiacetal, readily hydrolyzed to the carbonyl compound, but, for the ethers, involves the formation of a pseudoacetal, certainly more stable, making possible the simultaneous process of elimination of the β hydrogen.

The elimination seems to be favored in the cyclic ethers, where the carbonyl compound is recovered only in very small quantity and where the formation of aldehyde would require the opening of a ring. As mentioned above, the yields of acetaldehyde obtained in ethyl ether oxidation vary with conditions. They are higher at higher temperature, suggesting that the breakdown paths in eq 4′ do not have the same activation energy. They are higher at higher ether concentrations, presumably because the step $k_{2'}$ competes with the step

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

known from alcohol oxidations to occur readily.

It is worthy of note here that Sosnovsky[11] has reported that the cuprous bromide catalyzed reaction of *tert*-butyl peresters with ethers leads to the formation of acyloxy intermediates which decompose under the experimental conditions to the corresponding organic acids and unsaturated ethers.

The implication of our results can therefore be summarized.

I. A common type of mechanism is involved in the peroxydisulfate oxidation of alcohols and ethers.

II. The reaction of the α-oxyalkyl radicals with peroxydisulfate leads to the formation of pseudohemiacetal (from alcohols) or pseudoacetal (from ethers) intermediates. Therefore, the question concerning the transition state structure for k_3 seems to be answered; the chain lengths and rate laws are sufficiently similar as to lead to the conclusion that attack on peroxydisulfate by the α-oxyalkyl radical involves the carbon center.

III. The natures of the final products are related to the characteristics of the intermediates and to the experimental conditions. Yet, at the same time, the reaction kinetics are little influenced by the nature of the products.

Experimental Section

All chemicals not described below were reagent grade. Experiments carried out at B. U. utilized distilled water. Those carried out at M. S. C. utilized distilled–deionized water. B. & A. reagent $K_2S_2O_8$ was recrystallized twice from deionized water. Spectrophotometric grade dioxane (Aldrich) was used without further purification at B. U., whereas at M. S. C. Fisher reagent was purified as suggested by Fieser and Fieser.[12] Tetrahydrofuran (Mallinckrodt Analytical Reagent) was refluxed over KOH pellets and distilled before use. Ethyl ether (Allied, Reagent ACS) was distilled before use.

Kinetics were followed with a Cary 15 spectrophotometer (B. U.) or Beckman Acta V spectrophotometer (M. S. C.), or by the usual iodometric analysis. Rate constants were calculated as previously reported.[2,3] Rate constants calculated for duplicate runs with integrated plots usually agreed to ±5% and rate constants obtained from initial slopes varied by ±8%.

Products. The reaction mixture (an aqueous solution of $K_2S_2O_8$ and a tenfold molar excess of ether in a rubber-stoppered flask) was maintained at 60° in a thermostatic bath. Aliquots of the reacting solutions were withdrawn with a syringe, to prevent contact with air, at suitable time intervals and analyzed by vpc (Aerograph 200, F.I.D., column 15% SE-30 on 80/100 mesh A/W, DMCS Treste Chromosorb, 15 ft × 0.25 in. o.d.) and mass spectral (Hitachi Perkin-Elmer, RMU-6D single focusing, ionization 50 eV) techniques. The mass spectrometer and gas chromatograph were connected.

Compounds isolated were the 2,4-dinitrophenylhydrazone of acetaldehyde from ethyl ether oxidation and the osazone of glyoxal from the dioxane oxidation. Vinyl ethyl ether, *p*-dioxene, and 2,3-dihydrofuran (from ethyl ether, dioxane, and tetrahydrofuran, respectively) were identified by mass spectra. Both the mass spectra and gas chromatography showed abundant peaks not common to the reactant ethers. Details may be obtained on request.

Acknowledgments. We are pleased to acknowledge the support of the U. S. Air Force Office of Scientific Research (Grant 71-1961A) for continuing financial aid, of the Committee on International Exchange of Persons (Italy) for a travel grant (to R. C.), of Montclair State College for purchase of the Acta V spectrophotometer, and of the University of Padova for leaves of absence (to R. C. and F. D. F.). Mr. R. Campbell and Mr. G. Bida assisted with some of the measurements.

Registry No.—Peroxydisulfate, 15092-81-6; ethyl ether, 60-29-7; tetrahydrofuran, 109-99-9; dioxane, 123-91-1; copper, 7440-50-8.

References and Notes

(1) (a) Brown University (B. U.); (b) Montclair State College (M. S. C.).
(2) D. L. Ball, M. M. Crutchfield, and J. O. Edwards, *J. Org. Chem.*, **25**, 1599 (1960).
(3) (a) J. O. Edwards, A. R. Gallopo, and J. E. McIsaac, Jr., *J. Amer. Chem. Soc.*, **88**, 3891 (1966); (b) J. E. McIsaac, Jr., and J. O. Edwards, *J. Org. Chex.*, **34**, 2565 (1969); (c) A. R. Gallopo and J. O. Edwards, *ibid.*, **36**, 4089 (1971).
(4) For reviews on peroxydisulfate mechanisms, see (a) A. Haim and W. K. Wilmarth in "Peroxide Reaction Mechanisms," J. O. Edwards, Ed., Wiley-Interscience, New York, N. Y., 1962, p 176 ff; (b) D. A. House, *Chem. Rev.*, **62**, 185 (1972); (c) E. J. Behrman and J. E. McIsaac, Jr., *Mech. React. Sulfur Compounds*, **2**, 193 (1968); (d) E. P. Crematy, Ph.D. Thesis, University of Sydney, Australia, 1970.
(5) *Cf.* K. U. Ingold and B. P. Roberts, "Free-Radical Substitution Reactions," Wiley-Interscience, New York, N. Y., 1971, pp 148–200, and references cited therein.
(6) W. Buratti, G. P. Gardini, F. Minisci, F. Bertini, R. Galli, and M. Perchinunno, *Tetrahedron*, **27**, 3655 (1971).
(7) D. D. Mishra and S. Ghosh, *Proc. Nat. Inst. Sci. India, Part A*, **31**, 119 (1965).
(8) C. J. Battaglia, Ph.D. Thesis, Brown University, 1962.
(9) R. Curci, F. DiFuria, and J. O. Edwards, unpublished study at Brown Universtiy.
(10) The bulk of the data on the copper-catalyzed path is to be found in the M.A. Thesis of George M. Delano, Montclair State College, 1973.
(11) G. Sosnovsky, *Tetrahedron*, **13**, 241 (1961).
(12) L. F. Fieser and M. Fieser, "Reagents for Organic Chexistry," Wiley, New York, N. Y., 1967, p 333.

Reaction Kinetics of 2- and 3-Furoyl Chlorides with Anilines in Benzene

A. Arcoria,* S. Fisichella, G. Scarlata, and D. Sciotto

Institute of Industrial Chemistry of the University, Viale Andrea Doria 8, 95125 Catania, Italy

Received February 4, 1974

The reaction rates of 2- and 3-furoyl chlorides with substituted anilines have been measured in benzene at different temperatures. The reactions follow second-order kinetics. 2-Furoyl chloride reacts faster and 3-furoyl chloride slower than benzoyl chloride. The activation parameters and the slopes of the Hammett and Bronsted plots are similar to those of the reactions of benzoyl and 2- and 3-thenoyl chlorides with aniline. The reaction mechanism of 2- and 3-furoyl chlorides with aniline is the same as for the benzoylation reaction. A linear relationship is obtained plotting the log *k* for the reactions of 2-thenoyl, 3-thenoyl, 3-furoyl, and benzoyl chlorides with aniline against the infrared carbonyl stretching bands in CCl_4 of the acid chlorides.

Several studies have been carried out with the purpose of comparing the furan and thiophene rings reactivity with that of the benzene nucleus.

The acid-catalyzed rearrangement of substituted allyl alcohols shows that the furyl and thienyl groups behave as electron-donating substituents.[1] The carboxylic acids of furan and thiophene are stronger than unsubstituted benzoic acid indicating that the inductive electron-withdrawing effect of the heteroatoms is prevailing here.[2] In the esterification of the two isomeric 2- and 3-furoic acids,[3] in the acid-catalyzed hydrolysis of furan and thiophene carboxylic acid esters,[4] and in the alkaline hydrolysis of 2- and 3-