

solved in petroleum ether and cooled in ice. The gel which slowly formed was seeded with the crystalline product and allowed to stand at room temperature for 4 hr. During this time long, silky, white needles grew down from the surfaces of the gel and eventually there resulted a clear, fluid mother liquor and a beautifully crystalline product, melting at 52.8–54.8° (lit.⁹ m.p. 52–53°).

Triphenylcarbinol. A commercial sample melting at 159.8–161.0° (lit.¹⁰ m.p. 159°) was used.

Diphenylcarbinol. Eastman Kodak diphenylcarbinol was employed.

(9) E. Fischer and O. Fischer, *Ann.*, **194**, 265 (1878).

(10) E. Fischer and O. Fischer, *Ann.*, **194**, 271 (1878).

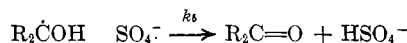
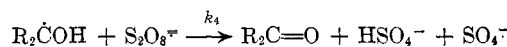
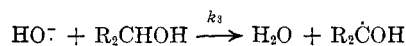
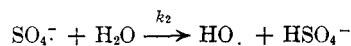
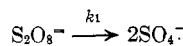
The Kinetics of the Persulfate Oxidation of 2-Propanol in the Presence of Other Organic Compounds

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Wiberg¹ has reported that allyl acetate decreases the first-order rate constant for the oxidation of 2-propanol (0.02 *M*) by potassium persulfate (0.02 *M*) from the value 0.84 hr.⁻¹ at 60° and pH 5 to the value observed in the absence of 2-propanol (0.014 hr.⁻¹). This fact was interpreted by Wiberg¹ as an "inhibition" by allyl acetate of a radical chain process, and the oxidation mechanism was represented by the following sequence of five irreversible free radical reactions, from which was derived the final rate law, $v = \sqrt{2k_1k_2k_4/k_5} [S_2O_8^{2-}]$:



Results

Experiments² recently carried out in these laboratories suggest that Wiberg's mechanism is incorrect for the following reasons. First of all, it is not true that allyl acetate reduces the first-order rate constant to that observed in the buffer solution alone. We have found that 0.04 *M* allyl acetate

reduces the rate only to approximately the value (0.063 hr.⁻¹) observed when it itself reacts with 0.02 *M* persulfate at pH 7 and 60°. This is 4.5 times the rate of disappearance of persulfate in the buffer alone. The results of Kolthoff, Meehan, and Carr³ also show that the reaction with allyl acetate is significantly faster (by about 40% at the half-time) than that with the buffer alone.

What is more significant, however, is the fact that 2-butanol (which hardly can be considered a "radical trap") produces the same type of result. We find that 0.02 *M* 2-butanol gives $k = 0.22$ hr.⁻¹ when alone in the buffer solution, and 0.02 *M* 2-propanol alone gives 0.85 hr.⁻¹, but the two together in the same solution give 0.30 hr.⁻¹ (Fig. 1).⁴

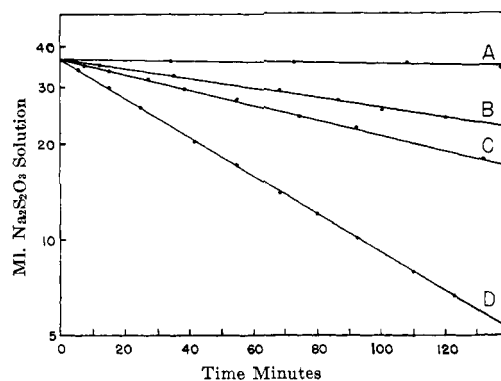


Fig. 1.—Rate of persulfate (0.02 *M*) oxidations in buffer solution at 60°: A, buffer alone; B, 2-butanol (0.02 *M*); C, 2-butanol (0.02 *M*) + 2-propanol (0.02 *M*); D, 2-propanol (0.02 *M*).

These data are summarized in Table I.

TABLE I
FIRST-ORDER RATE CONSTANTS FOR THE DISAPPEARANCE OF 0.02 *M* $K_2S_2O_8$ IN BUFFERED AQUEOUS SOLUTIONS OF VARIOUS ORGANIC COMPOUNDS AT 60°

Substrate	k (hr. ⁻¹)
Buffer solution alone	0.018
2-Propanol (0.02 <i>M</i>)	.84
Allyl acetate (0.04 <i>M</i>)	.060
Allyl acetate (0.04 <i>M</i>) + 2-propanol (0.02 <i>M</i>)	.063
2-Butanol (0.02 <i>M</i>)	.22
2-Butanol (0.02 <i>M</i>) + 2-propanol (0.02 <i>M</i>)	.30

We have also obtained similar results when equimolar concentrations of various other type organic compounds are present in the buffer solution together with isopropyl alcohol. Data for thiodiglycol sulfoxide at 70° are shown in Table II. We find, in general, that the more slowly the added compound is oxidized by persulfate, the more effective it is in diminishing the over-all rate of disap-

(1) K. B. Wiberg, *J. Am. Chem. Soc.*, **81**, 252 (1959).

(2) The experimental procedure was identical with that previously described (ref. 10). It should be noted that we encountered no difficulty in obtaining reproducible data, though such difficulty was reported by J. O. Edwards, *et al.* (ref. 6).

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

(4) It is seen from the first-order plots in Fig. 1 that the lines are perfectly straight with no evidence of the sigmoid character reported in ref. 6.

pearance of persulfate in solution of mixed substrates.

TABLE II

FIRST-ORDER RATE CONSTANTS FOR THE DISAPPEARANCE OF 0.02 M $K_2S_2O_8$ IN BUFFERED AQUEOUS SOLUTIONS OF VARIOUS ORGANIC COMPOUNDS AT 70°

Substrate	k (hr. ⁻¹)
Buffer solution alone	0.071
2-Propanol (0.05 M)	2.9
Thiodiglycol sulfoxide (0.05 M)	0.56
Thiodiglycol sulfoxide (0.05 M) + 2-propanol (0.05 M)	0.51

Discussion

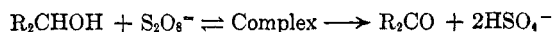
It is apparent from the above results that the diminution of the rate is due not to the trapping of free radicals, but instead to the formation, by the competing reductant⁵, of a stronger intermediate complex with the active oxidizing species than that which isopropyl alcohol forms with the oxidant. The rather unusual conclusions drawn recently by Edwards⁶ concerning the "inhibition" of persulfate oxidations by the addition of a sequestering agent (ethylenediamine tetraacetic acid, disodium salt) to eliminate traces of transition metal ions (mainly Cu^{++}), are almost certainly erroneous for the same reason: The sequestering agent is itself preferentially oxidized⁷ by the persulfate, and the active oxidizing species (possibly sulfur tetroxide, $\bar{O}_3S:\bar{O}^+$) is probably tied up, thus retarding the rate of disappearance of persulfate.⁸ It appears, therefore, that the "inhibition" of the reaction by this compound has little or nothing to do with the elimination of trace metal catalysis in persulfate oxidations.

Further evidence against a radical-chain mechanism for the persulfate oxidation of alcohols is the rather high activation energy⁹ (26 kcal./mole), and the fact that molecular oxygen¹⁰ has no effect whatever on the rate¹¹; even in the silver ion-catalyzed persulfate cleavage of glycols, strong evidence has been presented by Greenspan and Woodburn¹² that the reaction does not involve free radicals.

Turning to Wiberg's rate expression¹ for these

oxidations, we note that this equation does not involve the constant k_3 , which represents the rate of direct attack of the HO-radical on the alcohol molecule. Since this reaction is depicted as the only one in which an intact alcohol molecule participates, one might expect little or no variation of the rate when secondary alcohols other than 2-propanol are oxidized under the same conditions by persulfate.¹³ This is not what is observed experimentally, however, since the structure of the alcohol has a marked effect on the rate,¹⁴ as shown by the above-mentioned rate constants for 2-propanol and 2-butanol.

In any case, the proposed radical-chain mechanism does not in any way lead to the remarkable dependence of the initial first-order rate constant on the *initial* concentrations of alcohol and persulfate, which we have shown¹⁵ to be of the form $k = k_{max}[ROH]_0[S_2O_8^{2-}]_0 / (b + [ROH]_0)(c + [S_2O_8^{2-}]_0)$ where b and c are empirical constants. As already pointed out in our previous article,¹⁵ there is a close, but not exact, analogy between this rate expression and that for enzyme kinetics, thus strongly suggesting the existence of at least one equilibrium step in the reaction sequence, leading to the formation of a reactive intermediate complex which decomposes irreversibly to the observed oxidation products. In the case of a secondary alcohol this can be formulated



The intermediate complex is very likely one of the possible persulfate esters.¹⁶

(13) It is true that the rate constants k_1 and k_2 do appear in Wiberg's rate equation and these represent reactions of radicals formed by abstraction of a hydrogen atom from the carbinol carbon of the secondary alcohol. However, the bond dissociation energies of all these secondary alcohol radical species, and hence their reactivities, are nearly identical.

(14) B. W. Levitt and L. S. Levitt, Abstracts of Papers, Chicago Meeting, American Chemical Society, 5-P, September, 1958.

(15) E. R. Malinowski and L. S. Levitt, *J. Am. Chem. Soc.*, **80**, 5334 (1958).

(16) L. S. Levitt, *J. Org. Chem.*, **20**, 1297 (1955); see also ref. 9.

Photolysis of Nitrite Esters in Solution VI. Nitroso Dimers from Alicyclic Nitrites

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In a previous publication¹ it was established that cyclohexyl nitrite failed to undergo the Barton reaction.² The present study was undertaken to

(5) The competing organic compound is erroneously referred to as the "inhibitor" in Wiberg's paper (ref. 1).

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

(7) It was, indeed, found that persulfate slowly oxidized the sequestering agent (ref. 6).

(8) We assume that $S_2O_8^{2-}$ and SO_4 and their derivatives in the solution all titrate iodometrically as equivalent oxidizing agents, in the same fashion as do *t*-Bu-hypochlorite and the chromate esters.

(9) L. S. Levitt and E. R. Malinowski, *J. Am. Chem. Soc.*, **77**, 4517 (1955).

(10) E. Howard, Jr., and L. S. Levitt, *ibid.*, **75**, 6170 (1953).

(11) Nor has oxygen any effect on the rate of the persulfate oxidation of toluene. See A. Kailen and L. Olbrich, *Monatsh.*, **47**, 449 (1926).

(12) F. P. Greenspan and H. M. Woodburn, *J. Am. Chem. Soc.*, **76**, 6345 (1954).

(1) P. Kabasakalian and E. R. Townley, Part V, *J. Am. Chem. Soc.*, **84**, 2724 (1962).

(2) D. H. R. Barton, J. M. Beaton, L. E. Geller, and M. M. Pechet, *ibid.*, **82**, 2640 (1960).