

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, STEVENS INSTITUTE OF TECHNOLOGY]

Mechanism of Organic Oxidation in Aqueous Solution. I. Kinetics of the Persulfate Oxidation of Isopropyl Alcohol

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The kinetics of the persulfate oxidation of isopropyl alcohol were investigated at 60 and 50° in buffered aqueous solution of pH 8.0 and ionic strength 0.5. The rate of disappearance of persulfate was followed by iodometric titration. The reactions all were first order with respect to persulfate. A limiting rate is approached at higher initial alcohol concentrations, and the rate becomes independent of initial alcohol concentration. At lower initial concentrations of alcohol the rate exhibits a marked decrease and becomes proportional to the alcohol concentration. Thus the reaction is over-all first order at higher alcohol concentrations and over-all second order at lower concentrations. An empirical rate equation relating the observed rate constant to initial alcohol concentration is developed to fit the experimental data. On application of this equation to the data, good agreement between the calculated and experimental rate constants is obtained. An ionic mechanism involving a two-electron transfer, similar to that proposed for the persulfate oxidation of mercaptans and sulfoxides, is presented. From the proposed mechanism a rate equation of the required form is derived: $-d[S_2O_8^{2-}]/dt = k_2 K_1 [S_2O_8^{2-}] [ROH]_0 / ([SO_4^{2-}] (K_{-2} + [ROH]_0))$. The common characteristics of many organic oxidations in polar media are discussed.

Introduction

In a previous paper² we have shown that the rate of oxidation of diethyl and diphenyl sulfoxides by potassium persulfate at 80° in aqueous solution of pH 8.0 and ionic strength 0.5 is first order with respect to persulfate but independent of the sulfoxide concentration over the range studied (0.01–0.02 *M*). Later work³ has shown that the rate falls off rather sharply at somewhat lower sulfoxide concentrations, as was anticipated. In this low concentration range, then, the rate is proportional to the sulfoxide concentration and the reaction is therefore over-all second order. The same result has since been observed when thiodiglycol sulfoxide is oxidized by persulfate.⁴ In the persulfate oxidation of mercaptans⁵ a limiting rate also is attained, and since the same appears to be the case when sulfides⁶ are oxidized by persulfate, it was considered of interest to ascertain if this phenomenon extends to compounds other than those containing oxidizable sulfur.

We have chosen isopropyl alcohol for this purpose, since the oxidation product, acetone, is not itself subject to very rapid oxidation, and also because the kinetics of the chromic acid oxidation of this alcohol have been so thoroughly investigated.⁷ A kinetic study of the persulfate oxidation of methanol under conditions quite similar to ours has previously been carried out; the reaction order was found to be three-halves with respect to persulfate and one-half with respect to methanol concentration.⁸

Experimental

All kinetic runs were made at 60.0°, with an initial concentration of 0.02 *M* potassium persulfate, an ionic strength of 0.5, and pH 8.0. The samples were titrated iodometri-

cally. The isopropyl alcohol was Eastman Kodak Co. "spectro" grade.

The buffer solution and solution for titration of the samples were prepared in the same manner as previously described,² and the experimental procedure also was identical.

Results

In Fig. 1 are presented logarithmic plots of the kinetic data obtained in the oxidation of isopropyl alcohol at initial concentrations of 0.02, 0.01 and 0.005 *M*. Figure 2 gives similar plots for 0.20, 0.15, 0.10, 0.04, 0.006 and 0.003 *M* alcohol.

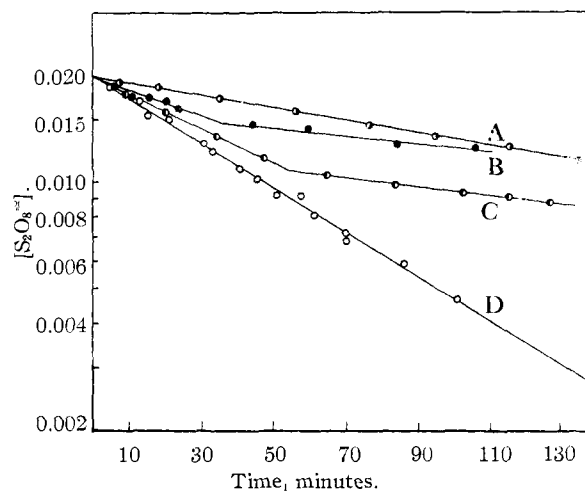


Fig. 1.—Persulfate oxidation of isopropyl alcohol: A, 0.02 *M* (50°); B, 0.005 *M* (60°); C, 0.010 *M* (60°); D, 0.020 *M* (two runs, 60°).

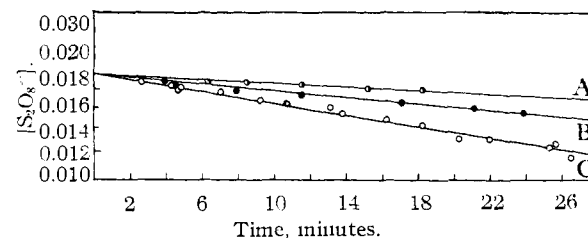


Fig. 2.—Persulfate oxidation of isopropyl alcohol at 60°: A, 0.003 *M*; B, 0.006 *M*; C, composite of four runs—0.20, 0.15, 0.10 and 0.04 *M*.

All the reactions are obviously and quite strictly first order with respect to persulfate. There are

(1) Done in partial fulfillment of the requirements for the M.S. degree at Stevens Institute of Technology.

(2) E. Howard, Jr., and L. S. Levitt, *THIS JOURNAL*, **75**, 6170 (1953).

(3) L. S. Levitt and E. Howard, Jr., unpublished results.

(4) L. S. Levitt and D. G. Ziebell, Abstracts of Papers (Organic Division), Cincinnati Meeting of A.C.S., April 7, 1955, p. 41N).

(5) R. L. Eager and C. A. Winkler, *Can. J. Research*, **B26**, 527 (1948).

(6) E. Larsson, *Trans. Chalmers Univ. Technol., Gothenberg*, **87**, 23 (1949).

(7) F. H. Westheimer and A. Novick, *J. Chem. Phys.*, **11**, 506 (1943); F. Holloway, M. Cohen and F. H. Westheimer, *THIS JOURNAL*, **73**, 65 (1951); A. Leo and F. H. Westheimer, *ibid.*, **74**, 4383 (1952).

(8) P. D. Bartlett and J. D. Cotman, Jr., *ibid.*, **71**, 1419 (1949).

points of inflection in the straight lines (Fig. 1) at approximately the concentration for which one would predict, from the stoichiometry of the reaction, that all the alcohol has been oxidized to ketone. The straight-line portion after the break in the curve may be interpreted as the rate of oxidation of the resulting ketone. The rate constant measured for the second portion of these reactions will be designated k' .

Table I gives the rate constants, k , observed for the oxidation of isopropyl alcohol at different initial concentrations. Also included in this table are the corrected rate constants, k_c , obtained by subtracting the value 0.018 hr.^{-1} (the first-order constant for the disappearance of persulfate when no alcohol is present in the solution⁹), and the observed and corrected rate constants, k' and k'_c , for the portion of reaction after the points of inflection.

TABLE I

FIRST-ORDER RATE CONSTANTS FOR THE OXIDATION OF ISOPROPYL ALCOHOL BY $0.02 \text{ M K}_2\text{S}_2\text{O}_8$ AT 60° IN AN AQUEOUS SOLUTION OF $\text{pH } 8.0$ AND IONIC STRENGTH 0.5

Initial concn. of $(\text{CH}_3)_2\text{CHOH}$, M	k , hr.^{-1}	k_c , hr.^{-1}	k' , hr.^{-1}	k'_c , hr.^{-1}
0.200	1.07	1.05
.150	1.07	1.05
.100	1.07	1.05
.040	1.05	1.03
.025	0.90	0.88
.020	.85	.83
.020	.83	.81
.015	.73	.71
.010	.65	.63	0.17	0.15
.006	.55	.53	.14	.12
.005	.48	.46	.15	.13
.003	.34	.32	.11	.092
.0	.018

These data are represented graphically in Fig. 3, in which the corrected initial rate constant, k_c , has been plotted *vs.* the initial alcohol concentration.

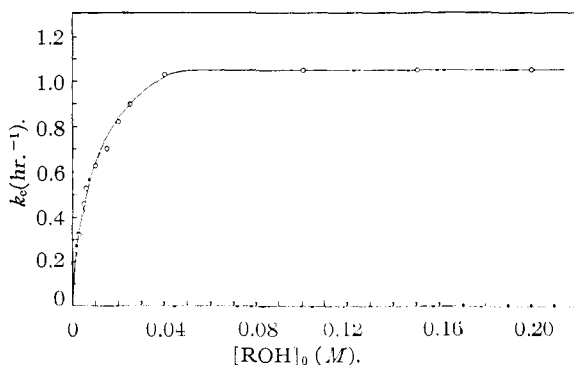


Fig. 3.—Variation of k_c with initial concentration of isopropyl alcohol; temp. 60° ; initial persulfate concentration 0.02 M .

Discussion

It is immediately evident from Fig. 3 that a limiting rate is attained at an initial alcohol concentration of about 0.05 M . Above this concentration the velocity of oxidation is independent of

alcohol concentration. At sufficiently low alcohol concentrations the rate exhibits a marked decrease. In this limited range, then, the rate is directly proportional to the concentration of alcohol. Thus the reaction would appear to be over-all second order at alcohol concentrations below 0.05 M and over-all first order at higher concentrations.

Form of the Rate Equation.—The following analysis of the data is essentially the same as that given previously⁹ for the persulfate oxidation of mercaptans.

The rate equation may be expressed in the following empirical form

$$-dP/dt = k_c P = k_{\max} A_0 P / (b + A_0) \quad (1)$$

in which k_c is the observed corrected first order rate constant, k_{\max} is the maximum or limiting rate constant, b is an empirical constant, A_0 , is the initial alcohol concentration, and P is the persulfate concentration.

Therefore, k_c is evidently given by

$$k_c = k_{\max} A_0 / (b + A_0) \quad (2)$$

It is seen that when $A_0 \gg b$

$$k_c = k_{\max} \quad (3)$$

and the rate is independent of alcohol concentration, and has reached the limiting value. When $A_0 \ll b$, however

$$k_c = k_{\max} A_0 / b \quad (4)$$

and the rate constant is proportional to the alcohol concentration. At intermediate concentrations, k_c is always a fraction of k_{\max} , the fraction being equal to $A_0 / (b + A_0)$. The constant b must have the units of concentration, and is, in fact, equal to the alcohol concentration at which the velocity of the reaction has attained one-half its limiting value; for when $A_0 = b$, then $k_c = k_{\max} A_0 / 2 A_0 = k_{\max} / 2$. It may be noted also, from eq. 4, that k_{\max} / b is the slope of the initial straight portion of the plot of k_c *vs.* A_0 (Fig. 3).

Evaluation of the Empirical Constants.—Both k_{\max} and b can be evaluated⁹ more accurately by rearranging eq. 2 to give

$$A_0 / k_c = b / k_{\max} + A_0 / k_{\max} \quad (5)$$

and plotting A_0 / k_c *vs.* A_0 , which results in a straight line with slope $1 / k_{\max}$ and intercept b / k_{\max} . From such a plot (Fig. 4), the slope is found to be 0.907 and therefore $k_{\max} = 1.10$; the intercept is equal to 6.4×10^{-3} , and thus $b = 7.0 \times 10^{-3}$.

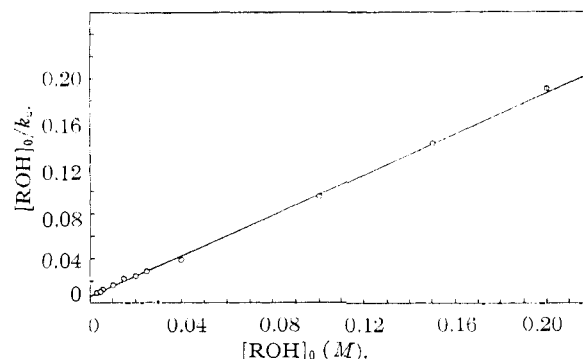


Fig. 4.—Test of equation 5.

(9) L. S. Levitt, *Can. J. Chem.*, **31**, 915 (1953).

Substituting the numerical values of k_{\max} and b in eq. 2, one obtains

$$k_c = \frac{1.10A_0}{0.0070 + A_0} \quad (6)$$

The observed rate constants, k_c , can thus be calculated from eq. 6. Table II gives a comparison of the observed values of k_c at different alcohol concentrations with the values computed from eq. 6. It is seen that the agreement is satisfactory.

TABLE II

OBSERVED RATE CONSTANTS FOR THE OXIDATION OF ISOPROPYL ALCOHOL AND THOSE CALCULATED FROM EQUATION 6

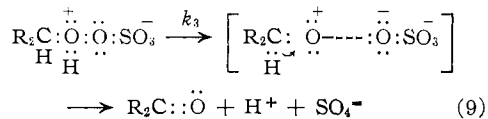
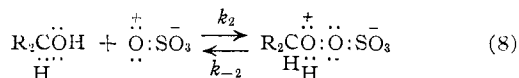
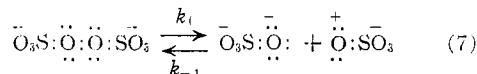
A_0 , concn. (M)	Obsd.	k_c Calcd.
0	0	0
0.003	0.32	0.33
.005	.46	.46
.006	.53	.51
.010	.63	.65
.015	.71	.75
.020	.82	.82
.025	.88	.86
.040	1.03	.94
.100	1.05	1.03
.150	1.05	1.05
.200	1.05	1.06

Activation Energy.—A kinetic run was made at 50.0° with a 0.02 *M* initial concentration of each of the reactants (Fig. 1). The rate constant (k_c) was 0.23 from which, together with the average value 0.82 observed at 60.0°, one obtains a value of 26 kcal./mole for the energy of activation. This may be compared with the following values observed in other persulfate oxidations: mercaptans,⁵ 26 kcal.; sulfoxides,² 25 kcal.; and water,² 32 kcal.

Proposed Mechanism.—The relatively high activation energies observed in all these oxidations afford evidence that the reactions are not of the radical-chain type. In addition, molecular oxygen has no effect on the rate of the persulfate oxidation of diethyl sulfoxide² nor of toluene.¹⁰

The nature of the rate dependence upon initial alcohol concentration suggests a mechanism involving one or more equilibrium steps and a rate-determining one. A mechanism for these reactions should also account for the retarding effect that sulfate ion has on the rate.¹⁰

The following mechanism, substantially in agreement with these requirements, is essentially the same as that postulated for the oxidation of sulfoxides,¹ mercaptans⁹ and of water⁹ by persulfate.

(10) A. Kailan and L. Olbrich, *Monatsh.*, **47**, 449 (1926).

It is assumed (eq. 7) that the persulfate ion dissociates by means of a heterolytic cleavage,^{9,11} into a sulfate ion and a molecule of sulfur tetroxide (SO₄), which is here considered to be the active oxidizing species. The electron deficient sulfur tetroxide then attacks the lone electron pair of the oxygen atom of the alcohol to form, reversibly, a monopersulfate ester (eq. 8) whose subsequent heterolytic decomposition gives rise to the reaction products (eq. 9).

The constant k_{-1} must be quite small since radioactive sulfate exchanges with persulfate very slowly.^{12,13} Free sulfur tetroxide, which is a powerful oxidizing agent,¹⁴ has been prepared.¹⁵ It is thought to be the anhydride of monopersulfuric (Caro's) acid (H₂SO₅), but reacts only slowly with water.¹⁶

Derivation of the Rate Equation.—From the foregoing mechanism, a rate equation of the required form (*cf.* eq. 1) may be derived in the following manner.

Since the limiting rate which is reached in these oxidations is a much lower limiting rate than that observed in the persulfate oxidation of mercaptans at the same temperature (calculated from the activation energy), one of the rate constants in the forward direction, other than k_1 , must be small; for if k_1 were the only slow and rate-determining reaction, then the same limiting rate should be observed in the oxidation of alcohols, sulfoxides, mercaptans and, in fact, any oxidizable substrate present. Hence it will be assumed that the decomposition of the ester (k_3) is a slow reaction with a rate of the same order of magnitude as k_1 . In such a case, the intermediate complex (ester) can accumulate to a considerable extent, and an equilibrium⁴ (rather than a steady state⁹) treatment is applicable.

The concentration of the ester will be represented as [X] and the equilibrium constants for eq. 7 and 8 are designated, respectively, K_1 and K_2 . Thus

$$K_1 = k_1/k_{-1} = [\text{SO}_4^-][\text{SO}_4]/[\text{S}_2\text{O}_8^{2-}] \quad (10)$$

and

$$K_2 = k_2/k_{-2} = [\text{X}]/[\text{SO}_4][\text{ROH}] \quad (11)$$

Equation 11 permits the concentration of the complex to be calculated in terms of the concentration of sulfur tetroxide and of alcohol. These concentrations, however, will not correspond to the initial concentrations, since appreciable amounts will have reacted to form the complex. Therefore, [SO₄] should be replaced by [SO₄] - [X], and [ROH] by [ROH]₀ - [X] (where the subscript zero refers to the initial concentration). Equation 11 then becomes

$$K_2 = [\text{X}]/([\text{ROH}]_0 - [\text{X}])([\text{SO}_4] - [\text{X}]) \quad (12)$$

This quadratic in [X] can be simplified by assuming

(11) I. M. Kolthoff and I. K. Miller, *THIS JOURNAL*, **73**, 3055 (1951).(12) F. C. Riesebois and A. H. W. Aten, Jr., *ibid.*, **74**, 2440 (1952).(13) H. Elkeles and C. Brosset, *Svensk Kem. Tid.*, **65**, 26 (1953).

(14) T. Moeller, "Inorganic Chemistry," John Wiley and Sons, Inc. New York, N. Y., 1953, p. 533.

(15) R. Schwarz and H. Achenbach, *Z. anorg. allgem. Chem.*, **219**, 271 (1934).

(16) H. J. Emeleus and J. S. Anderson, "Modern Aspects of Inorganic Chemistry," D. Van Nostrand Co., New York, N. Y., 1938, p. 349.

that $[\text{ROH}]_0 \gg [\text{SO}_4]$; then, since $[\text{X}]$ cannot exceed $[\text{SO}_4]$, it is negligible compared to $[\text{ROH}]_0$ but not negligible in comparison to $[\text{SO}_4]$. With this simplification eq. 12 may be written

$$K_2 = [\text{X}]/[\text{ROH}]_0([\text{SO}_4] - [\text{X}]) \quad (13)$$

from which $[\text{X}]$ is given by

$$[\text{X}] = K_2[\text{ROH}]_0[\text{SO}_4]/(K_2[\text{ROH}]_0 + 1) = \frac{[\text{ROH}]_0[\text{SO}_4]}{[\text{ROH}]_0 + K_{-2}} \quad (14)$$

Substituting in eq. 14 the equivalent of $[\text{SO}_4]$ given by eq. 10, and setting the over-all rate equal to $k_3\text{X}$, one obtains the final rate expression

$$\frac{-d[\text{S}_2\text{O}_8^{2-}]}{dt} = \frac{k_3 K_1 [\text{ROH}]_0 [\text{S}_2\text{O}_8^{2-}]}{[\text{SO}_4^{2-}](K_{-2} + [\text{ROH}]_0)} \quad (15)$$

It is seen that this equation is of the same form as the empirical expression (eq. 1), and that therefore

$$k_{\text{max}} = k_3 K_1 / [\text{SO}_4^{2-}] \quad (16)$$

and

$$b = K_{-2} = 1/K_2 \quad (17)$$

Thus the equilibrium constant K_2 for the formation of the ester X may be calculated from eq. 17. For isopropyl alcohol at 60° , $K_2 = 1/7.0 \times 10^{-3} = 1.4 \times 10^2$.

From eq. 16, the product $k_3 K_1$ can evidently be evaluated, but the rate constant k_3 and the equilibrium constant K_1 cannot be individually calculated from the data obtained in this investigation.

The Common Characteristics of Organic Oxidations in Polar Solution.—The mechanism postulated here for the persulfate oxidation of a secondary alcohol seems quite possibly to be the general mechanism by which alcohols (and perhaps many other organic compounds) are oxidized in polar media by the common strong inorganic oxidizing agents. The mechanistic courses of these reactions appear almost always to possess in common the following characteristics.

1. The active oxidizing species is rarely, if ever, a negative ion (e.g., NO_3^- , CrO_4^{2-} , $\text{S}_2\text{O}_8^{2-}$, ClO^- , IO_4^- , OOH^-), but appears to be most usually an electron deficient cationic species (e.g., NO_2^+ , CrO_2H^+ , Cl^+ , IO_3^+ , HO^+) or a highly polar molecule (e.g., NO_2 , CrO_3 , OSO_3) capable of undergoing a simple two-electron transfer¹⁷ (e.g., $\text{NO}_2 \rightarrow \text{NO}_2^-$; $\text{CrO}_3\text{H}^+ \rightarrow \text{CrO}_3\text{H}^-$; $\text{SO}_4 \rightarrow \text{SO}_4^{2-}$; $\text{Cl}^+ \rightarrow \text{Cl}^-$; $\text{IO}_3 \rightarrow \text{IO}_3^-$). These electrophilic substances are generally identical with those responsible for ordinary aromatic substitutions.

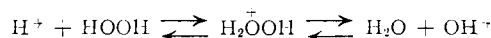
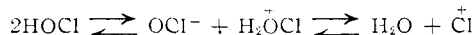
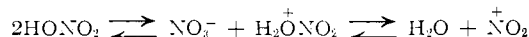
2. The positively charged atom of the active oxidizing species initially attacks a free electron pair of the reductant at a relatively electronegative site (e.g., $-\ddot{\text{O}}-$, $-\ddot{\text{S}}-$, $-\ddot{\text{X}}-$, $=\text{N}-$) forming a coordinate bond. The atom attacked gains a positive charge.

3. The positive charge is removed by expulsion of a positive fragment (usually H^+) or by combination with a readily available anion.

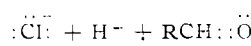
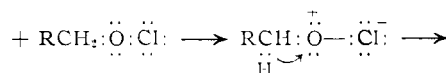
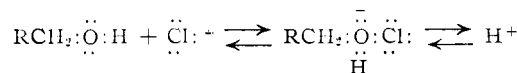
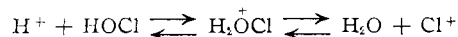
(17) Two electron oxidation-reduction reactions have been well established in many instances such as in the oxidation of sulfite by chlorate (J. Halperin and H. Taube, *THIS JOURNAL*, **74**, 375 (1952); A. C. Nison and K. B. Krauskopf, *ibid.*, **54**, 4606 (1932) and in the chromic acid oxidation of isopropyl alcohol (see ref. 7).

4. The oxidant begins to move off with the electron pair of the coordinate bond, resulting in a transition state in which an incipiently forming positive organic species simultaneously expels a second positive fragment or combines with a second negative ion.

All the common oxidizing agents are much more powerful in strongly acidic solutions principally, it seems, because of the ease with which the active oxidizing species are formed in the presence of a proton donor by reactions typified by the following examples

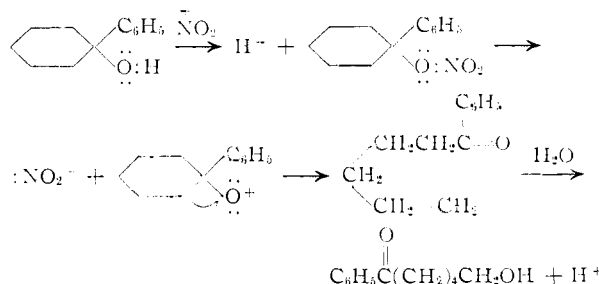


The four characteristics outlined above provide the common basis of many oxidation mechanisms previously proposed, such as the oxidation of mercaptans⁹ and sulfoxides⁴ by persulfate; the chromic acid oxidation of secondary alcohols⁷; the oxidation of alcohols¹⁸ and of formic acid¹⁹ by hypochlorous acid; and the oxidation of sulfides by acidic hydrogen peroxide.²⁰ One example, the hypochlorous acid oxidation of primary alcohols,¹⁸ will suffice for illustrative purposes. This reaction apparently proceeds through the intermediate formation of the hypochlorite ester in the following manner



These oxidations are first order in HOCl and alcohol and are accelerated by H^+ ion,¹⁸ because of the initial equilibrium in which Cl^+ is formed.

An example of the oxidative cleavage of a tertiary alcohol is the nitric acid oxidation of 1-phenylcyclohexanol, which almost certainly proceeds by way of the nitrate ester in the following manner



(18) G. Holst, *Swedish Kem. Tidn.*, **53**, 319 (1941).

(19) E. A. Shilov, A. I. Slyadnev and G. V. Kupinskaya, *Zhur. Obshchei Khim.*, **22**, 1497 (1952).

(20) S. D. Ross, *THIS JOURNAL*, **68**, 1484 (1946).

Further oxidation of the keto alcohol results in the final product, $C_6H_5CO(CH_2)_4COOH$.²¹

In the oxidation of alcohols, the reaction appears always to go through the intermediate stage of ester formation. For example, when CrO_3 , HNO_3 , $S_2O_8^{2-}$, $HOCl$ or HIO_4 is the oxidizing agent, the esters formed are, respectively, $ROCrO_3H$, $RONO_2$, $ROOSO_3H$, $ROCl$ and $ROIO_3$. These intermediate esters are relatively stable only when R is a tertiary alkyl group; the primary and secondary esters decompose in the cold and are violently explosive on heating.²² The reason for this is that the subsequent oxidative steps can proceed rapidly when a proton can be expelled from the incipiently forming ions $RCH_2:\ddot{O}^+$ or $R_2CH:\ddot{O}^+$, whereas a tertiary ester can expel only a carbonium ion (R^+) from $R_3C:\ddot{O}^+$, which is, energetically, more difficult to do. Thus, *t*-butyl hypochlorite,²³ and chromate²⁴ are surprisingly stable.

The formation of carbonium ions in the oxidative cleavage of tertiary alcohols, ketones and acids²⁵

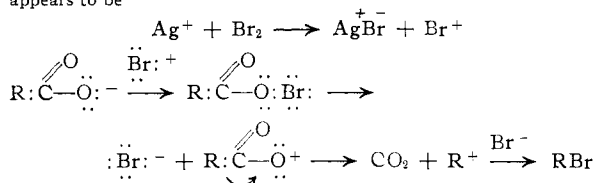
(21) L. F. Fieser and M. Fieser, "Organic Chemistry," D. C. Heath and Co., Boston, Mass., 1950, p. 709.

(22) F. C. Whitmore, "Organic Chemistry," D. Van Nostrand, New York, N. Y., 1951, p. 156-158.

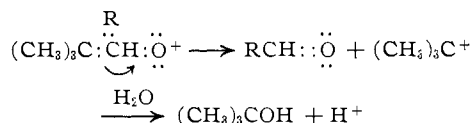
(23) D. Ginsberg, *Experientia*, **7**, 95 (1951); L. F. Audrieth, E. Colton and M. M. Jones, *THIS JOURNAL*, **76**, 1428 (1954).

(24) R. V. Oppenauer and H. Oberrauch, *Anales Asoc. quim. argentina*, **37**, 246 (1949).

(25) Oxidative decarboxylation of acids may well proceed through the formation of an acyl ester, $RCOOX$, as the intermediate. The acyl nitrates and bisulfates have been isolated, though they are very unstable (ref. 22, p. 293). A typical example of such an oxidative fission is the decarboxylation of silver salts, $RCOO^-Ag^+$, by reaction with bromine (E. Maekawa, *C. A.*, **48**, 1245f (1954)). The mechanism appears to be



is implicit in the generalized approach to organic oxidation presented here. Even primary and secondary alcohols might be expected to expel carbonium ions in competition with proton ejection when the carbonium ion (such as $(CH_3)_3C^+$ or $C_6H_5CH_2^+$) is one that can be formed readily because of its relative stability. Such cleavage actually has been observed in the case of chromic acid oxidation of methyl-*t*-butylcarbinol to *t*-butyl alcohol and acetaldehyde²⁶ and of phenyl-*t*-butylcarbinol to *t*-butyl alcohol and benzaldehyde.²⁷ The mechanism of the cleavage is easily explained on the basis of the present view, and may be simply represented as



If carbonium ions of sufficiently long half-life are actually ejected from molecules undergoing oxidative fission of C-C bonds, one might expect that rearrangements involving certain of them would have been noted. Such molecular rearrangements have in fact been observed, for example in the chromic acid oxidation of cyclooctatetraene²⁸ to *p*-phthalic acid, and in the permanganate oxidation of camphene²⁹ to camphenic acid.³⁰ Both of these reactions may be explained³¹ readily on the basis outlined here.

(26) W. A. Mosher and F. C. Whitmore, *THIS JOURNAL*, **70**, 2544 (1948).

(27) A. Leo and F. H. Westheimer, *ibid.*, **74**, 4383 (1952).

(28) E. E. Royals, "Advanced Organic Chemistry," Prentice-Hall, Inc., New York, N. Y., 1954, p. 547.

(29) Ref. 22, p. 581.

(30) A striking confirmation of the carbonium ion nature of the cleaved group has been established recently in the chromic acid oxidation of *l*-3-methyl-3-phenyl-2-pentanol, in which the expelled carbonium ion was completely racemized to give *d,l*-2-phenyl-2-butanol (W. A. Mosher and S. Duckworth, Abstracts of Papers, Cincinnati Meeting of A.C.S., April 2, 1955, p. 46N).

(31) L. S. Levitt, *J. Org. Chem.*, in press.

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NOTES

The Oxidation of Tungsten Carbide

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Tungsten carbide powder is known to burn in air, but information about the ignition temperature and rate of combustion seems lacking. For analytical combustion it is common to use high temperatures, oxygen and a flux, although rapid direct combustion can be achieved at approximately 1400° in oxygen.¹ The present thermobalance studies show that fine tungsten carbide powder begins to oxidize rapidly

(1) E. L. Simons, J. E. Fagel, Jr., and E. W. Balis, *Anal. Chem.*, in press.

in air at 500 to 520°, and can be burned completely at 529°.

The materials used were: (1) a tungsten carbide powder supplied by the Carboloy Department of the General Electric Company. This material contained $6.24 \pm 0.04\%$ C, or 0.11% more than theoretical.¹ (2) A macrocrystalline tungsten carbide obtained from the Wah Chang Corporation. Samples of these materials were weighed into porcelain crucibles and heated at a rate of 300°/hr. (unless otherwise noted) in a pen-recording Chevenard thermobalance. This instrument, manufactured by Société Adamel, is similar in principle and operation to that described by Duval.²

The curves from four experiments are shown in

(2) C. Duval, "Inorganic Thermogravimetric Analysis," Elsevier Publishing Co., New York, N. Y., 1953, Part 1, Chapter 2.