The Mechanism of Oxidation of Alcohols by Aqueous Bromine

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Abstract: The pH–rate profile for the oxidation of 2-propanol by Br_2 indicates the presence of two independent mechanisms. At pH 2–6, the rate is invariant with pH and the predominant mechanism is direct attack of Br_2 on the 2-propanol. At pH 7–9, the rate follows [HOBr] and appears to involve intermediate formation of ROBr. Both mechanisms are closely related to the oxidative cleavage of ethers by Br_2 and involve as a unifying feature the abstraction of an electron pair from the oxygen by bromine and the loss of an α-hydrogen as H^+.

In the previous paper[1] it was shown that ethers are oxidized by aqueous Br_2. The pH–rate profile for diisopropyl ether parallels Br_2 concentration, and this leads to constant rates at pH 1–4 and a rapidly decreasing rate above pH 7. The exact pH at which [Br_2] starts decreasing (due to conversion to HOBr and ultimately OBr^-) depends on the over-all stoichiometric concentration of Br_2 and is about pH 4 for 10^{-3} M Br_2.

In contrast to the results with diisopropyl ether, the pH–rate profile for the oxidation of 2-propanol starts to rise around a pH of 6, as shown in Figure 1. This contrasting behavior of alcohol and ether has led us to examine in more detail the mechanism of oxidation of alcohols by Br_2.

The rate law for the oxidation of ethanol,[2-4] 2-propanol,[5] and cyclohexanol[6] has been shown to be

$$-d[ROH]/dt = k_2[ROH][Br_2] \qquad (1)$$

The rate is pH invariant in the pH 1–4 region[4,5] and begins to increase with increasing pH around pH 6.[4] This was rationalized on the basis that a new reaction path had appeared which involved oxidation of RO^- by Br_2. Such a path would lead to

$$d \log k_2/d\ (pH) = 1 \qquad (2)$$

and the limited data from pH 6 to 7 seemed to support such a rationalization.[4] However, this explanation ignored the fact that [Br_2] was sharply decreasing in this same region due to the Br_2–HOBr equilibrium and that this effect would exactly cancel the effect of eq 2.

The more complete pH–rate profile in Figure 1 shows that in the pH 6–9 region the rate closely parallels [HOBr]. It is concluded that the total rate law is

$$-d[ROH]/dt = k_2[Br_2][ROH] + k_2'\ [HOBr][ROH] \qquad (3)$$

and that the two mechanisms are direct attack of Br_2 on alcohol and decomposition of alkyl hypobromite.

The transition state for the direct attack of Br_2 on ROH is pictured as I. The transition state for the mechanism proceeding through ROBr is II. Both transition states are similar to the transition state III, for the oxidative cleavage of ethers by Br_2. The close

similarity between I, II, and III provides a unifying concept of such oxidations.
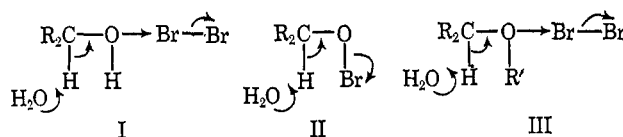
These transition states also resemble that proposed by Westheimer (IV) for the oxidation of alcohols by chromic acid.[7] A further parallel between chromic acid oxidations and Br_2 oxidations is that the alcohols have a faster mechanism, *via* the chromate and hypobromite esters, than the ethers.[8] This was once implied to be due to a change in mechanism,[8] but we feel that the chromic acid oxidation of ethers is much like the chromic acid oxidation of alcohols, and these bear the same relation to each other as III does to II.

The views presented above are not in accord with past proposals on the mechanism of the Br_2 oxidation of alcohols. The proposal that RO^- accounts for the pH–rate profile[4] has already been shown to be incorrect. Kaplan rejected a ROBr intermediate on the basis that $k_H:k_D$ for the Br_2 oxidation of CH_3CD_2OH was 3–4.[9] Since the decomposition of ROBr could, and probably does, involve the breaking of a C–H bond in the rate-determining step, the rejection of ROBr intermediates was unwarranted.

A direct hydride abstraction by Br_2 was advanced[5] on the basis that $k_H:k_D$ ratios were similar for $(CH_3)_2$-CDOH, 2.94, and $CH_3CDOHCH_2F$, 2.83. This conclusion was based on the view that $k_H:k_D$ ratios are more sensitive to substituent for proton transfers than hydride transfers.[5] To us, this does not seem to follow from the theory of primary kinetic isotope effects, and it certainly has not been supported by experiment.

Our view is that these $k_H:k_D$ ratios of 2–4 reflect the breaking of a C–H bond in the transition state, as depicted in I–III. It is of interest that $k_H:k_D$ for the chromic acid oxidation of $(CH_3)_2CDOH$ is comparable, being 6.6 at 25°.[7]

A cyclic transition state, IV, was proposed for the oxidation of cyclohexanol.[6] This structure reflects the earlier view[5,9] that the oxidation is a hydride abstraction. Of course, IV can be altered to have the

(1) N. Deno and N. H. Potter, *J. Am. Chem. Soc.*, **89**, 3550 (1967).
(2) S. Bugarszky, *Z. Physik. Chem.*, **38**, 561 (1901); **71**, 705 (1910).
(3) L. Farkas, B. Perlmutter, and O. Schächter, *J. Am. Chem. Soc.*, **71**, 2829 (1949).
(4) B. Perlmutter-Hayman and V. Weissman, *ibid.*, **84**, 2323 (1962).
(5) C. G. Swain, R. A. Wiles, and R. F. W. Bader, *ibid.*, **83**, 1945 (1961).
(6) I. R. L. Barker, W. G. Overend, and C. W. Rees, *Chem. Ind.* (London), 558 (1961).

(7) R. Stewart, "Oxidation Mechanisms," W. A. Benjamin, Inc., New York, N. Y., 1964, pp 37–48, gives a review of the work of F. H. Westheimer.
(8) 2-Propanol reacts 1500 times faster than diisopropyl ether (R. Brownell, A. Leo, Y. W. Chang, and F. H. Westheimer, *J. Am. Chem. Soc.*, **82**, 406 (1960)).
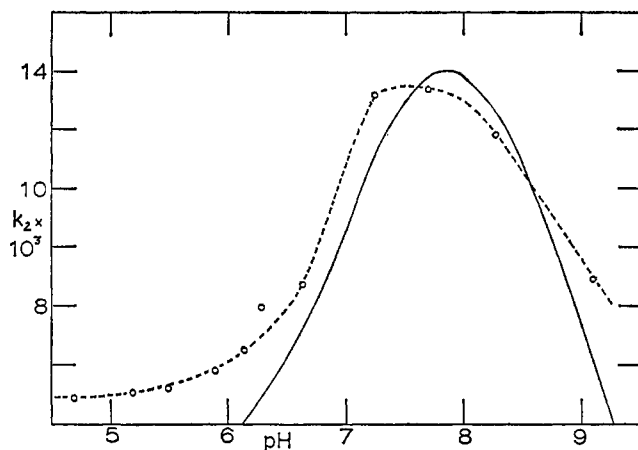(9) L. Kaplan, *ibid.*, **80**, 2639 (1958).

Figure 1. The dotted line with the experimental points (circles) are k_2, 1. mole^{-1} sec^{-1}, for the oxidation of 2-propanol by aqueous Br$_2$ in the dark at 25.0°. The solid line is [HOBr] calculated for 0.100 M NaBr and 1.80 $\times$ 10^{-3} M stoichiometric HOBr (or Br$_2$) concentration. The value of 1.80 $\times$ 10^{-3} M was chosen to bring the curves into closest coincidence since any offset vertically is of no significance.

electrons flow in the opposite direction or to have a five-membered ring with a Br–O interaction. These modifications would be similar to I, and there is little to distinguish them from I.

IV
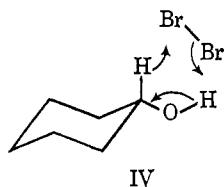
2-Propyl acetate and ethyl acetate were directly oxidized by aqueous Br$_2$ at pH 5. The oxidation took placed prior to hydrolysis. The reactions were slower than the attack on alcohols and ethers, which presumably reflects the weaker basicity of esters[10] and the reduced availability of the electron pairs on oxygen.

It is concluded that primary and secondary alkyl groups in alcohols, ethers, or esters are susceptible to oxidation on the α-carbon by aqueous Br$_2$.

Experimental Section

Rates of Oxidation of 2-Propanol. The calculation of the second-order rate constants and their method of measurement

(10) E. M. Arnett, *Progr. Phys. Org. Chem.*, **1**, 223 (1963).

were identical with those used with diisopropyl ether.[1] Most of the data appears in Figure 1. Not shown in Figure 1 is a value of 2.59 $\times$ 10^{-3} 1. mole^{-1} sec^{-1} at pH 3.85. At every pH the [Br$_2$]$_0$ was 10^{-3} M, [NaBr] was 0.100 M, and the total concentration of buffer was 0.100 M. From pH 3.85 to 6.65, the buffer was sodium acetate–acetic acid. From pH 7.49 to 8.30 it was borax–boric acid. At pH 9.10 it was borax.

The curve for [HOBr] in Figure 1 was computed from

$$2 \times 10^{-9} = [\text{H}^+][\text{OBr}^-]/[\text{HOBr}] \qquad (4)^{11}$$

and

$$9 \times 10^{-9} = [\text{H}^+][\text{Br}^-][\text{HOBr}]/[\text{Br}_2] \qquad (5)^{12}$$

Oxidation of Ethyl Acetate and 2-Propyl Acetate. A mixture of 0.01 mole of ethyl acetate and 0.02 mole of Br$_2$ was monitored by pmr spectroscopy at 25°. The pH was held at 4.6 by an acetate buffer and occasional additions of aqueous KOH. After 7 days, the ethyl bands had completely disappeared and were replaced by those of acetate.

A concern was that the ester was hydrolyzing and that the Br$_2$ oxidation was occurring on the ethanol produced by hydrolysis. This concern was dispelled by monitoring the pmr spectrum in the absence of Br$_2$. After 7 days no change had occurred and, in particular, no bands of ethanol had appeared.

An identical experiment, including the test for hydrolysis, was conducted on 2-propyl acetate. Again the ester was oxidized, as evidenced by the disappearance of ester bands and the appearance of the acetone band. Reaction was complete in 7 days.

Table I. Rate Constants for the Oxidation of 2-Propanol by Br$_2$ at 25.0°

pH^a	10^3k_2, 1. mole^{-1} sec^{-1}	pH^a	10^3k_2, 1. mole^{-1} sec^{-1}
3.85	2.59	6.30	5.95
4.70	2.93	6.65	6.70
5.20	3.06	7.49	13.2
5.50	3.20	7.72	13.4
5.85	3.81	8.30	11.8
6.15	4.47	9.10	6.84

^{a} Values of pH from 3.85 to 6.65 were achieved by 0.10 M acetate buffers. Values from 7.49 to 9.10 were achieved by 0.10 M borax–boric acid buffers. All runs contained 0.10 M NaBr.

(11) E. A. Shilov, *J. Am. Chem. Soc.*, **60**, 490 (1938).
(12) See the discussion in footnote 19 of ref 1 for the basis for this choice.