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THE MECHANISM OF OXIDATION OF ALCOHOLS BY BROMINE

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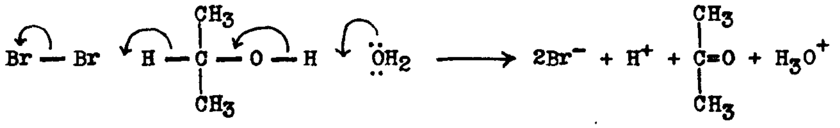
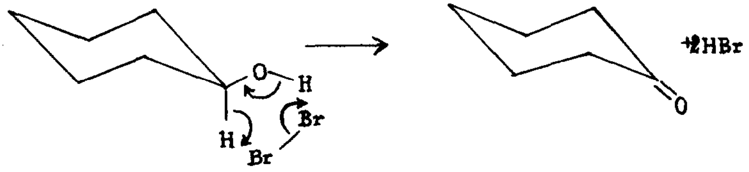
Swain, Wiles and Bader(1) have proposed a mechanism (A) for the bromine oxidation of alcohols, involving a rate-determining hydride transfer from carbon, followed by a fast proton removal from oxygen, or a partly concerted process in which the proton removal is synchronous with the hydride transfer. In contrast to this acyclic mechanism, Barker, Overend and Rees(2) have proposed a cyclic transition state (B) for the bromine oxidation of cyclohexanol.



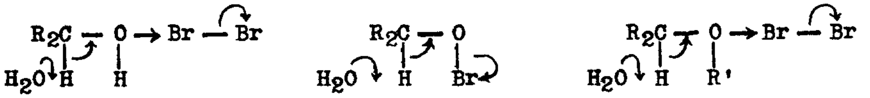
$$Br-Br\quad H-\underset{CH_3}{\overset{CH_3}{C}}-O-H\quad \ddot{O}H_2 \longrightarrow 2Br^- + H^+ + \underset{CH_3}{\overset{CH_3}{C}}=O + H_3O^+$$

(A)



(B)

Deno and Potter(3) have, however, in a recent publication questioned the validity of both the mechanisms. According to these authors, the bromine oxidation of propanol-2 is invariant with pH between pH 2-6 and involves a direct attack of Br_2 on the alcohol. At pH 7-9, the reaction is said to involve HOBr and the intermediate formation of ROBr. The oxidative cleavage of ethers by Br_2 is held to be related to the oxidation of alcohols. They propose an alternative mechanism (C) for the oxidation of alcohols involving the abstraction of an electron pair from the oxygen by bromine and the loss of the secondary hydrogen as a proton.


(C)

This mechanism is suggested on an apparent parallelism between chromic acid oxidation and bromine oxidation of alcohols and ethers. As against the ethers the alcohols are supposed to have a faster mechanism through the chromate and hypobromite esters. However, it is relevant to point out here that while propanol-2 reacts 1500 times faster than diisopropyl ether(4), the rate constants for the Br_2 oxidation of propanol-2 and diisopropyl ether at 25°C and pH = 4.6 are identical(5).

The most striking difference between the two mechanisms (A) or (B) and (C) is the type of hydrogen transfer: the former requires a hydride anion transfer and the latter assumes a proton transfer. Hence electronegative groups would be expected to retard the oxidation if mechanism (A) or (B) is correct and accelerate it if mechanism (C) holds.

We wish to report in this communication, the results of rate measurements on the bromine oxidation of a number of alcohols with suitable electronegative and electropositive substituents. The table presented here consists of the bimolecular rate constants for the oxidation of the alcohols in 70% $HO\bar{A}c$ - 30% H_2O at 40°C and at a pH = 4.0. The bromine concentration was 0.003M and the concentration of the tribromide ion was negligible in this poorly ionizing solvent. Preliminary runs on the bromination of the products viz., ketones were found to be very slow compared to the oxidation.

It is evident that the influence of polar groups on the oxidation rate is very pronounced. The replacement of the hydrogen atom on the methyl group of propanol-2 by $-Cl$, $-Br$, $-OCH_3$, $-OC_4H_9(n)$, $-C_6H_5$; - groups of strong electronegative character reduce the rate considerably, while α-alkyl groups, with their characteristic +I effect accelerate the oxidation. A quantitative correlation also exists between the electronegativities of the substituents and the rates of oxidation as revealed by a fair linearity in a Taft(6) plot (Fig.). The magnitude of ρ^* from this plot is -2.6.

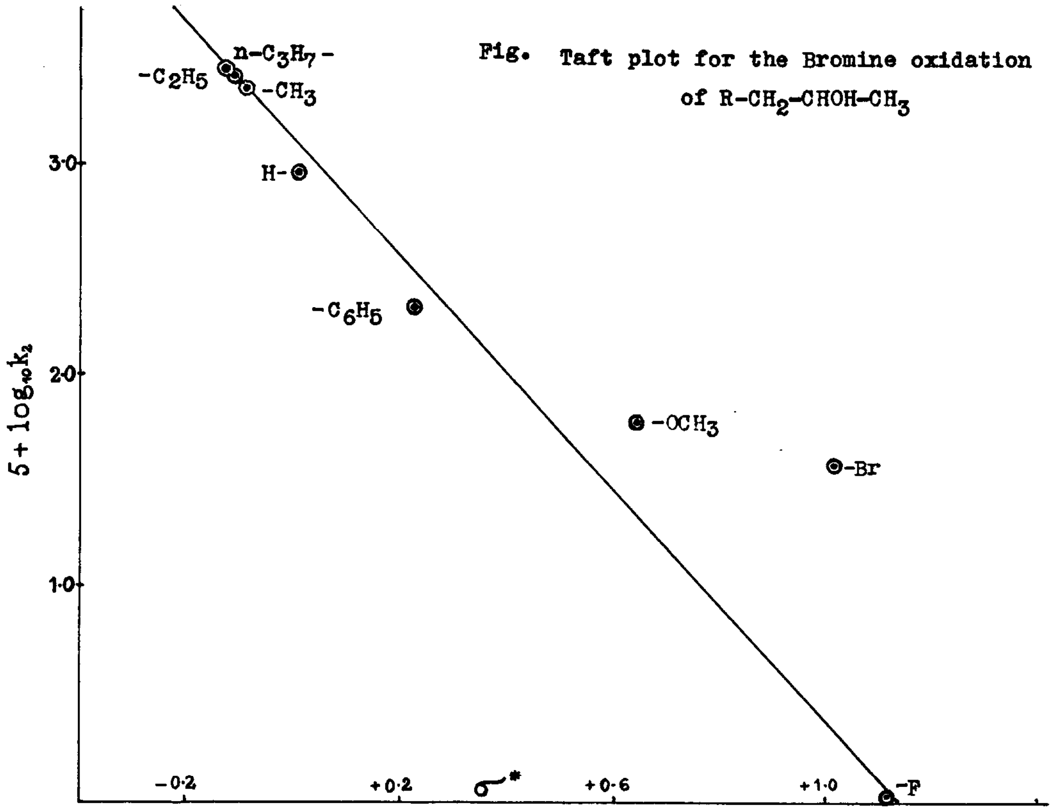


Fig. Taft plot for the Bromine oxidation of $R-CH_2-CHOH-CH_3$

TABLE

Compound	$k_2 \times 10^3$ litre-mole^{-1}sec^{-1}
Propanol-2	9.9680
Butanol-2	23.6000
Pentanol-2	27.2700
Pentanol-3	44.9300
Hexanol-2	27.8600
1-Bromo propanol-2	0.3844
1,3-Dichloro propanol-2	0.4046
1-Phenyl propanol-2	2.6000
1-Methoxy propanol-2	0.6240
1-n-Butoxy propanol-2	0.4490

The negative ρ^* value points to an electron deficient carbon centre in the transition state for the reaction. It is already known that an α-fluoro substituent reduces the rate of Br_2 oxidation of propanol-2 by over 1000 times(1). A computed value for this alcohol has been included in the Taft plot.

While other arguments can be advanced to explain the negative ρ^* value, the simplest explanation seems to us to be a rate-determining loss of the secondary hydrogen as an anion. A hypobromite ester formation is not likely to be susceptible to any considerable structural influence as in other alcohol - inorganic acid esterifications(7,8). The large negative ρ^* value can thus arise only out of the differential effects of the substituents in the rate-determining step. It may also be pointed out that in the oxidative cleavage of benzyl methyl ethers by aqueous bromine Deno and Potter(5) obtain a σ-ρ plot with a marked curvature but still with a large negative slope.

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REFERENCES

1. Swain, C.G., Wiles, R.A. and Bader, R.F.W., J.Amer.Chem.Soc., 83, 1945, (1961)
2. Barker, I.R.L., Overend, W.G. and Rees, C.W., J.Chem.Soc., 3263, (1964)
3. Deno, N.C. and Potter, N.H., J.Amer.Chem.Soc., 89, 3555, (1967)
4. Leo, R.B.A., Chang, Y.W. and Westheimer, F.H., J.Amer.Chem.Soc., 82, 406, (1960)
5. Deno, N.C. and Potter, N.H., J.Amer.Chem.Soc., 89, 3550, (1967)
6. Taft, R.W., ''Steric effects in organic chemistry'' Edited by Newman, M.S., p.556, Wiles, New York, (1956)
7. Deno, N.C. and Newman, M.S., J.Amer.Chem.Soc., 72, 3852, (1950)
8. Kläning, U., Acta.Chem.Scand., 11, 1313, (1957)
ibid., 12, 576, (1958)

J.Chem.Soc., 3204, (1961)