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THE KINETICS OF OXIDATION OF SECONDARY ALCOHOLS BY POTASSIUM BROMATE

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As part of a comprehensive scheme on the oxidation mechanisms of organic substrates by various oxidants, we investigated the kinetics of the oxidation of secondary alcohols by potassium bromate. Conventionally one uses this oxidant in an acid medium in the presence of potassium bromide in the molecular proportions of 1:5 in which case the active oxidant is essentially molecular bromine. In fact this was a primary obstacle in studying the pure BrO_3^- oxidation in an acid medium, as the Br^- formed as the reduction product as it collects in the system, it produces Br_2 and ettatic kinetics result. We had shown in an earlier publication that the Br^- can be kept in solution either as unionised $HgBr_2$ or as a complexed bromo mercuri species (most probably as $HgBr_4^{2-}$) by the addition of a calculated quantity of mercuric acetate[1]. We adopted the same technique here too, to study the pure bromate oxidation of secondary alcohols for the first time but have come upon certain peculiar results which we communicate here.

The kinetics were investigated by following the disappearance of bromate by iodometry and the data reveal second order kinetics — first with respect to both the bromate and the alcohol. This was unequivocally established for both BrO_3^- and the alcohol by standard methods and the reaction also exhibits a total second order when the alcohol and BrO_3^- were taken in near equal quantities. But the most surprising aspect of the kinetic data is that alcohols (R-CHOH-R') with varying substituents in the R and R' groups (propan-2-ol, butan-2-ol, pentan-2-ol, heptan-2-ol, octan-2-ol, α-phenyl ethyl alcohol and benzhydrol) give very nearly the same <u>second order rate constant</u>. It was only when the alcohol was of a totally different structure (such as fluoren-9-ol) or had a strongly electron-withdrawing substituent as the -Cl or $-NO_2$ group the reaction exhibited any variation in rate.

TABLE

Effect of substituents and pH on the rate of oxidation of secondary alcohols by $KBrO_3$

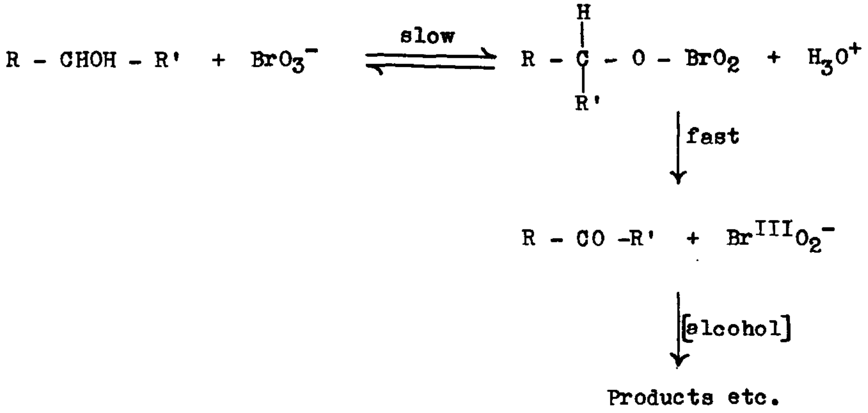
Solvent: 50% $\overline{HOAc}$ - 50% H_2O

ALCOHOL	$k_2 \times 10^4$ litre-mole^{-1} sec^{-1}		
	pH = 0.70 (50°C)	pH = 2.0 (55°C)	pH = 3.0 (55°C)
Propan-2-ol	26.4 36.8*	3.84	2.30
Butan-2-ol	27.6	4.25	..
Pentan-2-ol	30.3	4.00	..
Octan-2-ol	30.9	4.84	..
1:3-Dichloro-propan-2-ol	8.50	..	..
α-Phenyl ethyl alcohol	29.2 36.0*	4.62	2.91
Benzhydrol	52.0	10.5	..
Fluoren-9-ol	445†	..	..
2-Nitro-fluoren-9-ol	96.8†	..	..

* at 55°C ; † in 60% $\overline{HOAc}$ - 40% H_2O

Even here the variation in rate is not considerable. In many other systems employing Br_2, NBS etc., (essentially two-electron oxidants), the substrate alcohols do exhibit profound polar effects$^{2,3,4)}$. Even with Ce^{4+}, V^{5+} and Co^{3+} (ordinarily one-electron oxidants), substituent effects are prominent$^{5)}$.

We feel that the observed kinetics and the insensitivity to structural variation can only be explained if one assumes the slow formation of an alkyl bromate in the rate-determining step,which subsequently undergoes a fast decomposition.



$$R-CHOH-R' + BrO_3^- \xrightleftharpoons{\text{slow}} R-\overset{H}{\underset{R'}{\overset{|}{\underset{|}{C}}}}-O-BrO_2 + H_3O^+$$

$$\big\downarrow \text{fast}$$

$$R-CO-R' + Br^{III}O_2^-$$

$$\big\downarrow [\text{alcohol}]$$

Products etc.

The equilibrium formation of the alkyl bromate esters is most likely to be insensitive to structural changes by analogy with ester formation with sulphuric acid and chromic acid$^{6,7)}$. One will necessarily have to assume that these esters decompose spontaneously, rapidly, unlike the chromate esters, which are known to decompose in a slow step$^{8)}$. When the alcohol moiety has a strongly electron-withdrawing group (as in 1:3-dichloro-propan-2-ol or 2-nitro-fluoren-9-ol), the ester-decomposition step may become slow leading to a lowered rate.

Further the oxidation reaction which exhibits a second order dependence on the hydrogen ion concentration, has not only a lowered rate at higher pH, but exhibits a small dependence of rate on alcohol structure. Probably at higher pH, the unimolecular decomposition of the bromate ester tends to become the rate-limiting step. At pH > 3.5 however, the reaction is very sluggish and very little oxidation takes place.

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