Tetrahedron Vol. 44, No. 8, pp. 2225 to 2231, 1988
Printed in Great Britain.

0040-4020/88 $3.00+.00
Pergamon Press plc

KINETICS AND MECHANISM OF OXIDATION OF SOME ARYL ALCOHOLS BY ACID BROMATE

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(*Received in UK* 2 *February* 1988)

Abstract - The kinetics of oxidation of some substituted benzyl alcohols as well as the unsubstituted one by bromate ion in hydrochloric acid medium has been suggested. The results indicate that the reaction takes place by way of intermediate ester formation. Methoxy compounds react at much faster rates than the corresponding nitro substituted derivatives. The thermodynamic values associated with the equilibrium step and also for the slow step have been evaluated. A mechanism consistent with the experimental observations has been suggested.

The mechanism of the oxidations of some alcohols by metal ion oxidants like Cr(VI)[1-4], V(V)[5,6], Co(III)[7,8], Mn(VII)[9-12] and Ce(IV)[13-15] have been reported. These reactions also exhibit a variety of mechanistic behaviours. Moreover, the similarities and differences in the behaviour between different oxidants have been shown.

Potassium bromate is known to be a powerful oxidant[16] in acid solution [$E^{o} = 1.52$ volts at 25°C]. The bromate ion oxidations of Mn(II)[17], Np(V)[18], VO_2^{+2} [19], Fe(II)[20] and Ir(III)[21] have been studied. The kinetics and mechanism of the oxidation of some aromatic aldehydes by acid bromate has been investigated and mechanism involving the formation of an unstable bromate ester which decomposes to the reaction products has been suggested[22]. The kinetics of oxidations of some aliphatic alcohols by the same oxidant have been studied[23] in dilute sulphuric acid-acetic acid medium. The kinetics and mechanism of the oxidation of benzyl alcohol and some substituted benzyl alcohols by potassium bromate in aqueous hydrochloric acid medium have been studied and are reported in this communication.

EXPERIMENTAL

Reagents Benzyl alcohol (BDH) was purified by distillation just before use. The substituted aryl methanols (7 through 15 ; Table 2) were prepared as follows. To an ice-cold solution of the substituted benzaldehyde (5g) in pure methanol (40 ml) was added sodium borohydride (2g) in small portions with stirring and the mixture was left at room temperature for 12-16 h with occasional stirring. It was then cooled, acidified with concentrated hydrochloric acid and extracted with a mixture of ether and benzene (1:1 ; v/v). The organic layer was dried with sodium sulphate, the solvent was removed on a steam bath, and the residue was distilled to furnish the substituted aryl methanol in 70-90 % yield depending on the substitutions.

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The ir spectra indicated the absence of aldehydes in these products. Potassium bromate, mercuric acetate, potassium iodide, sodium chloride and hydrochloric acid were of BDH grade. All the solutions were prepared in doubly distilled water.

Rate Measurements The kinetics were followed iodometrically by monitoring the concentration of bromate at regular intervals of time to a starch end-point. Each reaction was conducted under pseudo first order condition, in which the substrate was in large excess to that of the bromate. During the oxidation interference by the liberated bromine was prevented by adding a calculated quantity of mercuric acetate whereby the bromide ion formed from potassium bromate was removed as a complex. It has been observed that mercuric acetate is inert towards the oxidation of the alcohols. The pseudo-first order rate constants were then calculated from log $[BrO_3^-]$ vs. 't' plots which were reproducible to within ± 3 % .

Product Analysis The product analysis of the acid-bromate oxidation of benzyl alcohol has been done in which the reaction mixture has the following composition:

$[PhCH_2OH] = 6.0 \times 10^{-2}M$, $[KBrO_3] = 1 \times 10^{-3}M$, $[HCl] = 1.0$ M and $[Hg(OAc)_2] = 1x10^{-2}M$.

Two sets of experiments were carried out. In the first set, the reaction mixture (250 ml) of the oxidation product of benzyl alcohol was set at 25°C for 40 minutes. It was treated with excess of 2,4-dinitrophenylhydrazine hydrochloride solution and left for half an hour. The precipitate was filtered, washed with water and dried (100 mg). It was chromatographed over neutral alumina [Brockman (12 g) ; column length - 6"], eluted with dry benzene and the solvent was removed to furnish a crystalline 2,4-D.N.P. derivative, which was recrystallized from rectified spirit to yield orange crystals (10 mg.), m.p. 235°-236°C(d), m.m.p. remained undepressed on admixture with an authentic 2,4-D.N.P. derivative of benzaldehyde. The ir spectra of these 2,4-D.N.P. derivatives were also identical in all respect.

In another set of experiment the aforementioned reaction mixture (250 ml) was kept at 25°C for 144 hours and analysed in the following way. To a few drops of it was added potassium iodide followed by starch. The absence of violet colour indicated that potassium bromate was completely consumed. The remaining portion of the reaction mixture was extracted with chloroform (4x20 ml), washed with water (10 ml), then extracted with saturated sodium bicarbonate solution (2x10 ml; preserved), again washed with water (2x10 ml), dried (Na_2SO_4) and solvent removed. The residue on treatment with 2,4-dinitrophenylhydrazine hydrochloride gave the 2,4-D.N.P. derivative of benzaldehyde (200 mg, crude) which was confirmed by the aforementioned method.

The preserved bicarbonate extract was acidified with concentrated hydrochloric acid (congo red), extracted with chloroform (3x10 ml), washed with water (10 ml), dried (Na_2SO_4) and solvent was removed. The absence of any residue confirmed that benzoic acid was not formed.

RESULTS

Effect of Variation of Reactant Concentration The pseudo first order rate constants (k_{obs}) were calculated at various $[Bromate]_0$ but at constant $[substrate]_0$, $[H^+]_0$ and temperature. The values of k_{obs} were found to be $(5.0 \pm 0.1)x10^{-3}$ (s^{-1}) for a variation of $[Bromate]_0$ from 0.5×10^{-3} to 4.0×10^{-3} M at constant $[PhCH_2OH]_0$, $[H^+]_0$ and temperature of 1.6×10^{-2} M, 1M and 20°C respectively. The results indicated that rate is constant in the oxidant range studied. The pseudo first order rate constant (k_{obs}) were determined at different $[substrate]_0$ but at constant $[Bromate]_0$, $[H^+]_0$, ionic strength ($\mu = 1.0M$) and temperature. The plots of log k_{obs} against log $[substrate]_0$, gave slopes which are less than unity. This is to be expected if the reactions take place through the formation of intermediate complex followed by its decomposition to give the products. The plots of $1/k_{obs}$ against $1/[substrate]_0$ are linear making different intercepts on the Y-axis at different temperatures (Figure 1). From the slope and intercept of each line, the values of Ke, the equilibrium constant, were calculated to be 69.4, 42.9, 25.8 and 17.65 at 15°, 20°, 25° and 30°C respectively. The enthalpy change associated with the complex formation for each reaction was thus calculated from the plot of log Ke against 1/T plot followed by the estimation of ΔS from the relation,

$$\log Ke = \frac{1}{2.303\,R}\left(\Delta S - \frac{\Delta H}{T}\right)$$

The values of ΔH and ΔS associated with complex formation are -67 k J mol^{-1} and -197.5 J K^{-1} mol^{-1} respectively.

Effect of Variation of Hydrochloric Acid Concentration The effect of variation of $[H^+]_0$ on the rate of oxidation was studied at an ionic strength of 1.0 M. The oxidation rates increased with the increase in the acidity. The plot of k_{obs} against $[H^+]_0$ is linear passing through the origin. The quotients, $k_{obs}/[H^+]_0$ at different acidities have been calculated and are recorded in Table 1. These indicate that the dependence of rate on $[H^+]_0$ is unity.

Effect of Changing Acetic Acid Concentration The pseudo first order rate constant was determined by changing the composition of acetic acid in the reaction mixture but at constant concentration of other reactants. The rate increases from 2.16×10^{-3} (s^{-1}) to 3.45×10^{-3} (s^{-1}) for a change of acetic acid concentration from 12 % to 50 % (v/v). The values are recorded in Table 2.

Influence of Temperature The influence of temperature on the rate of reaction was studied at different temperatures but at constant concentration of reactants, and acidity. The values of k_d calculated from the double reciprocal plots are 5.88×10^{-3}, 11.1×10^{-3}, 25.0×10^{-3} and 66.7×10^{-3} (s^{-1}) at 15°, 20°, 25° and 30°C respectively. The plots of log (k_d/T) against $1/T$ yielded straight line in case of benzyl alcohol, from the slope of which $\Delta H^{\neq}$ followed by $\Delta S^{\neq}$ was calculated from the relation

$$\log\left(\frac{k_d}{T}\right) = \left[\log\frac{k}{h} + \frac{\Delta S^{\neq}}{2.303\,R}\right] - \frac{\Delta H^{\neq}}{2.303\,RT}$$

The respective activation parameters are 114.8 k J mol^{-1} and 110.6 J K^{-1} mol^{-1}.

Effect of Substituents The oxidation reactions involving a series of substituted benzyl alcohols and the oxidant were carried out under comparable condition of experiments. Since the substituted benzyl alcohols were very much less soluble in water than benzyl alcohol, all the solutions were made in 12 % acetic acid in water (v/v). Since benzhydrol and o-nitrobenzyl alcohol were insoluble in 12 % acetic acid solution, their oxidations were studied in 50 % acetic acid solution in water (v/v). The results presented in Table 2 indicate that unsubstituted benzyl alcohol reacts at a faster rate than benzhydrol. Again, of different nuclear substituted benzyl alcohols, methoxy compounds react at much faster rates than the corresponding nitro- and chloro- substituted derivatives. For the m- and p- substituted alcohols, the pseudo-first order rate constants generally follow the order, methoxy > chloro > nitro. However, the results of o-substituted chloro- and nitro- derivatives cannot be compared with those mentioned above since the oxidation of o-nitrobenzyl alcohol was carried out in 50 % acetic acid (v/v). An attempt was also made to correlate the values of k_d and K_e of the different meta- and para-substituted benzyl alcohols. The first Hammett plot[24] of log k_d against log K_e is linear with a negative slope (Figure 2) which exhibits a linear free energy relationship between these two steps.

DISCUSSION

The salient feature of the results described are summarised as follows. The rate of oxidation is found to be first order with respect to $[BrO_3^-]$ but the order with respect to the [Benzyl alcohol] is less than unity. The rate increases linearly with an increase in the acidity. The alcohols are all oxidized to give carbonyl compounds. The oxidation of alcohols by bromate failed to induce polymerisation of acrylonitrile.

The reaction may occur between alkoxide ion and oxidant or between alkoxonium ion and oxidant. Since in acid medium (1.0M) the concentration of alkoxide ion is very small, this cannot be considered as reactive reductant. Alcohols are also known to be weak proton acceptors and converted to alkoxonium ion in the presence of high concentration of mineral acids. Since the reaction has been carried out in 1 M HCl, it is very unlikely that the alcohols will be protonated under the condition of the experiment in acid medium. The molecular form of the substrate and not the anion or protonated form reacts with the oxidant. The kinetic evidence indicates that an intermediate bromate ester (I) is formed prior to electron transfer followed by the decomposition of the ester (I) to give carbonyl compound and $HBrO_2$. Since $HBrO_2$ is highly reactive it reacts further with alcohol as shown below.

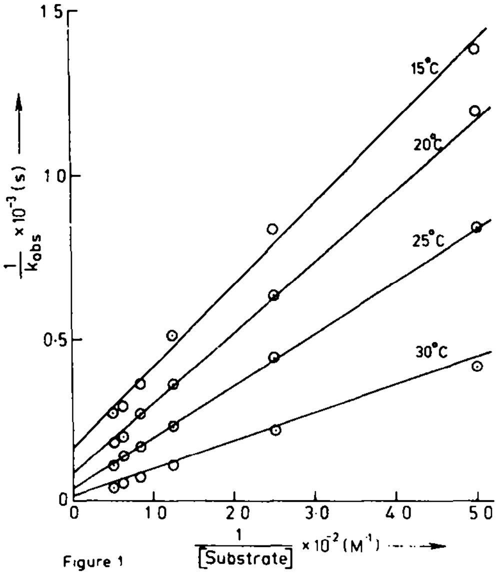


Figure 1. Variation of pseudo-first order rate constant with substrate concentration. Plots of $1/k_{obs}$ versus $1/[\text{substrate}]$ at different temperatures. $[KBrO_3] = 1 \times 10^{-3}$ M, $[H^+] = 1$ M, $[Hg(OAc)_2] = 1 \times 10^{-2}$ M.

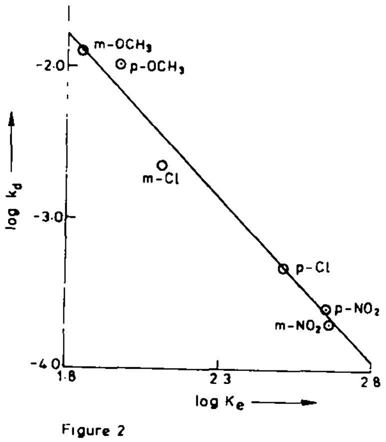
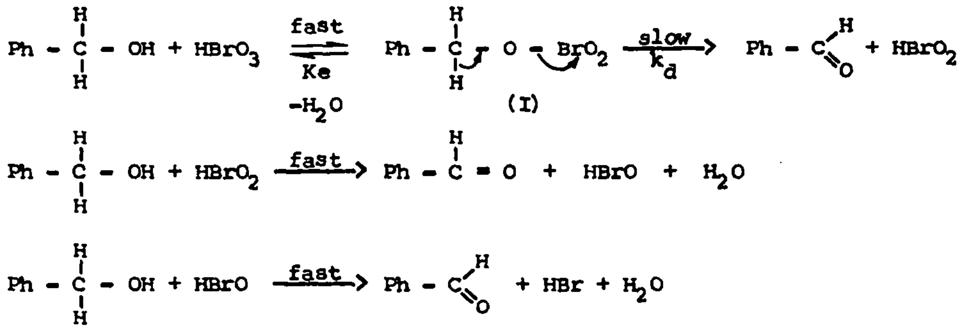


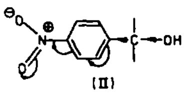
Figure 2. Linear free energy relationship. The first Hammett plot of log k_d versus log K_e.

Scheme 1

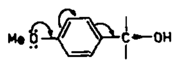


The structures II through V will illustrate the expected resonance as well as the inductive effects exhibited by substituents at the *para* position of the benzyl alcohol.

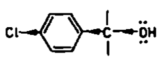
The mechanism of the oxidation of different *para* substituted alcohols (II-V) by bromate ion in hydrochloric acid medium may be explained through the formation of intermediate ester as shown in Scheme 2. The bromate ester (VI) then decomposes to give the corresponding substituted benzaldehydes as has been suggested in Scheme 1.



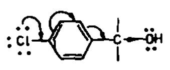
(II)



(III)

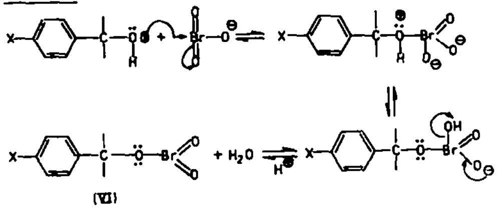


(IV)



(V)

Scheme 2



(VI)

If this mode of esterification is correct, then the electron attracting or electron repelling character of X (X = $-NO_2$, -Cl and -OMe) will have a dramatic influence on the rate of intermediate bromate ester formation. Thus, when X is nitro group (i.e. an electron attracting group), the lone pair of an oxygen atom of the alcoholic -OH group will be less available for the bromate ester formation, as has been shown in II. The formation of intermediate ester is not favoured and so k_{obs} will be low. Conversely when X is methoxy group, the lone pair on the oxygen of the alcoholic -OH group is more available due to electron repelling nature of the methoxy group leading to the enhancement of the intermediate bromate ester formation as has been shown in III. Consequently both the resonance and inductive effect favours the formation of the intermediate bromate ester which is supported by its high k_{obs} value in the case of methoxy substituted compounds. When X is chlorine, two opposing influences i.e. resonance and inductive effects compete for the preference where resonance effect overcomes the inductive effect

Table 1. Variation of Pseudo First Order Rate Constant with $[H^+]$.
$[KBrO_3] = 1.0 \times 10^{-3}$ M, [Benzyl alcohol] $= 1.0 \times 10^{-2}$ M
$\mu = 1.0$ M, Temp $= 20^\circ$C

$[H^+]$ (M)	$k_{obs} \times 10^4$ (s^{-1})	$\frac{k_{obs}}{[H^+]} \times 10^3$
0.1	3.9	3.90
0.2	7.0	3.50
0.4	13.0	3.25
0.6	19.7	3.30
0.8	28.3	3.53
1.0	37.9	3.79

Table 2. Pseudo First Order Rate Constants of The Acid Bromate Oxidation of Different Aromatic Alcohols.
$[KBrO_3] = 1 \times 10^{-3}$ M, Substrate $= 8 \times 10^{-3}$ M,
[HCl] $= 1.0$ M, Temperature : 20°C

No.	Substrate	% HOAc (v/v)	$k_{obs} \times 10^3$ (s^{-1})	k_{rel}
1	Benzyl alcohol	12	2.16	1
2	"	20	2.54	1.17
3	"	30	2.97	1.37
4	"	40	3.20	1.48
5	"	50	3.45	1.59
6	Benzhydrol	"	1.68	0.49*
7	*o*-Nitrobenzyl alcohol	"	0.45	0.13*
8	*m*-Nitrobenzyl alcohol	12	0.19	0.088
9	*p*-Nitrobenzyl alcohol	"	0.235	0.109
10	*o*-Chlorobenzyl alcohol	"	0.24	0.111
11	*m*-Chlorobenzyl alcohol	"	1.14	0.53
12	*p*-Chlorobenzyl alcohol	"	0.32	0.148
13	*o*-Methoxybenzyl alcohol	"	12.0	5.55
14	*m*-Methoxybenzyl alcohol	"	10.0	4.63
15	*p*-Methoxybenzyl alcohol	"	8.7	4.03

* k_{rel} calculated with respect to k_{obs} in 50 % HOAc

and the rate is expected to be intermediate between the nitro- and methoxy-derivatives. In benzhydrol probably the steric hindrance due to the second phenyl group on the carbinol carbon makes the bromate ester formation less favourable than in benzyl alcohol, thereby decreasing the value of k_{obs} in benzhydrol.

The oxidation of benzyl alcohol by bromate ion in acid medium has been shown to occur to give benzaldehyde. It is known that carbonyl compounds are oxidized by different oxidants via their hydrates and the oxidation of benzaldehyde by bromate takes place smoothly in acetic acid medium[22] (> 50 % , v/v). However, some preliminary experiments involving benzaldehyde and acid bromate were carried out and the reactions were too slow to be studied in 1.0 M HCl and at [Benzaldehyde] $\leqslant 1.0 \times 10^{-3}$ M. Thus further oxidation of benzaldehyde under the condition of the experiments seems unlikely.

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