Kinetics and Mechanism of Oxidation of Formamide and Dimethyl Formamide by Potassium Bromate in Aqueous Perchloric Acid Medium

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Most of the kinetic studies on the oxidation of amides are restricted to peroxo-disulphate and Tl^{III} oxidations in aqueous medium[1,2]. Various workers studied the kinetics of oxidation of DMF[3] and formamide[4] by Tl^{III}, acetamide and formamide by Ag^{II} [5] and aliphatic amides[6] by Ce^{IV}. Amides undergo oxidation by two distinctive mechanisms : (i) direct oxidation and (ii) hydrolysis followed by the oxidation of hydrolysis products. It is therefore of interest to see which one of the above routes is possible when bromate is the oxidant in perchloric acid medium. The present communication reports the results of the reaction of formamide and dimethyl formamide with potassium bromate in perchloric acid medium.

Results and Discussion

Under the conditions $[HCONH_2] \gg [BrO_3^-]$ the order in $[BrO_3^-]$ was unity as seen from the linear plot of log $a/(a-x)$ vs time (where a is the initial $[BrO_3^-]$ and $(a-x)$ the $[BrO_3^-]$ at time t). The order in $[HCONH_2]$ was also found to be unity as seen from the slope of the linear plot of log k_{obs} vs log $[HCONH_2]$. The double reciprocal plot of $1/k_{obs}$ vs $1/[HCONH_2]$ was also linear with no intercept on Y-axis indicating that no stable complex is formed between the oxidant and the substrate. Addition of acrylonitrile to the reaction mixture did not show any polymerisation thus indicating the absence of free radicals.

The important point in bromate oxidations is to establish the reactive species that participates in a given reaction. Bromate exists in acid medium in various forms like BrO_3^-, $HBrO_3$, $H_2BrO_3^+$, BrO_2^+ etc[7]. In the present study the reactive species was established by studying the effect of $[H^+]$, [HOAc] and [Salt] on rate. The rate increased with increase in $[H^+]$ and the order in $[H^+]$ was found to be one indicating that only one proton is involved in the reaction as per the equilibrium reaction (1),

$$H^+ + BrO_3^- \rightleftharpoons HBrO_3 \qquad (1)$$
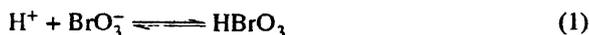
The rate increased with increase in % composition of HOAc and a linear plot was obtained between log k_{obs} and $(D-1)/(2D + 1)$ (where D is the dielectric constant of the medium) with a negative slope, indicating that the reaction is of dipole-dipole type. The rate increased marginally with increase in $[KClO_4]$ and [KCl] suggesting that the reaction is not an ion-ion type but may be of ion-dipole or dipole-

dipole type. Hence, it may be concluded that $HBrO_3$ is the most probable reactive species in the present study.

Amides are known to get hydrolysed in strong acids and bases. The rate of hydrolysis of formamide is expected to be greater than all other aliphatic amides due to mesomeric effects. It was necessary to find out the extent of hydrolysis[8] of formamide at 50°. The hydrolysis at this temperature was fast as compared to the redox reaction. For a typical run at $[HCONH_2] = 0.050$ mol dm^{-3} and $[HClO_4]_t = 0.500$ mol dm^{-3}, the hydrolysis was half-complete within 6 min of mixing the reactants as compared to the half-life of 2 h for the reduction of Br^V at $[BrO_3^-] = 5.00 \times 10^{-3}$ mol dm^{-3}, $[HCONH_2]_t = 0.050$ mol dm^{-3} and $[HClO_4] = 0.500$ mol dm^{-3} at 50°. Since the hydrolysis is rapid and over in the initial stages of the reaction, the concentration of formic acid formed when $[HClO_4] > [Amide]_t$ was taken to be equal to $[Amide]_t$. However, when $[Amide]_t > [HClO_4]_t$, the amount of amide hydrolysed, i.e. formic acid formed was taken as equal to the amount of perchloric acid initially taken, and the concentration of unhydrolysed amide remaining, [Amide] was equal to the difference of $[Amide]_t$ and $[HClO_4]_t$. In the present investigation, $[HClO_4]$ was several times in excess of [amide] and hence the amount of formic acid formed is assumed to be equal to the concentration of the amide taken initially.

Another point to be ascertained is whether the oxidation process involves the oxidation of hydrolysis product, i.e. formic acid alone or the oxidation of both formic acid and unhydrolysed formamide. To verify this point, the oxidation of formic acid as well as DMF was studied. The rate of reaction was in the order of $HCONH_2 \simeq HCOOH > DMF$ (Table 1). In order to verify that the formamide oxidation

Substrate	$k' \cdot 10^3$ dm^3 mol^{-1} s^{-1}	E_{exp}	ΔH^*	ΔG^*	ΔS^*
		kJ mol^{-1}			J K^{-1} mol^{-1}
Formamide	1.92	76.5	73.8	96.0	−68.7
Formic acid^a	2.04	71.8	69.1	96.1	−83.5
DMF	0.087	95.7	93.0	98.3	−16.4

$^a[HCOOH + NH_4^+] = 5.00 \times 10^{-2}$ mol dm^{-3}.

is in fact the oxidation of formic acid, the oxidation of formic acid in the presence of ammonia was studied. From the results (Table 1) it is seen that the rate of formic acid is of similar order of magnitude as that for formamide oxidation. Further, the addition of ammonia does not affect the rate of reaction. Also, the unit order in [oxidant] and [substrate] indicates that probably the same mechanism is operative in both formic acid and formamide oxidations.

It is also possible that some amount of unhydrolysed formamide also got oxidised along with the hydrolysis product HCOOH. This possibility was ruled out by studying the DMF oxidation where the rate was negligible compared to that of $HCONH_2$ under the conditions employed. If unhydrolysed amide is getting oxidised, then the reactivity of DMF should be greater than that of formamide due to mesomeric effect of methyl groups. However, such trend was not observed in the present study. And also the alkylation of nitrogen reduces the rate of hydrolysis of amide to a greater extent by inductive effects and this explains the low reactivity of DMF. Hence, it is concluded that the rate of hydrolysis of amide is faster than the rate of oxidation and only the hydrolysis product, i.e. formic acid gets oxidised by the acid bromate.

Based on the above observations the probable mechanism can be written as

$$H^+ + HBrO_3^- \underset{fast}{\overset{K_1}{\rightleftharpoons}} HBrO_3$$

$$HCONH_2 + H_3O^+ \underset{fast}{\overset{K_2}{\rightleftharpoons}} HCOOH + NH_4^+$$

$$HCOOH + HBrO_3 \underset{fast}{\overset{k_3}{\longrightarrow}} CO_2 + H_2O + HBrO_2$$
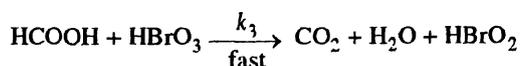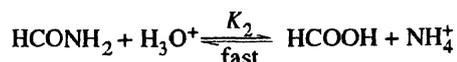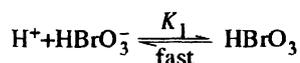
$HBrO_2$ thus formed gets further reduced to Br^- in subsequent oxidation steps. From the above mechanism the rate of disappearance of $[BrO_3^-]$ is given by equation (2),

$$\frac{d[BrO_3^-]}{dt} = k_3[HBrO_3][HCOOH] \tag{2}$$

Substituting the values of $[HBrO_3]$ and $[HCOOH]$.

$$-\frac{d[BrO_3^-]}{dt} = k_3 K_1 K_2 [BrO_3^-][HCONH_2][H^+] \tag{3}$$

which explains all the experimental results obtained.

The effect of temperature on rate was studied at four different temperatures (318, 323, 328 and 333 K). The activation parameters for all the three substrates determined are presented in Table 1. From the data it is clear that the energy of activation for formamide is similar to that for the oxidation of HCOOH in the presence of NH_3. Further-

more, the entropy of activation in these two cases is negative and of similar magnitude. These points suggest that the mechanisms for two reactions are similar. The constancy of ΔG^* values indicates that probably the same type of mechanism is operative in all the three cases, viz. formamide, formic acid and DMF oxidations.

Experimental

Formamide, dimethyl formamide and perchloric acid (all AnalaR) were used as such. Mercuric acetate (E. Merck) was used to fix the bromide ions in the system. The reaction was followed by estimating the unreacted bromate iodometrically. All the experiments were conducted under pseudo-first order conditions using ten-fold excess of the substrate over oxidant and all the kinetic parameters were studied with formamide as the substrate. Preliminary studies showed that the reaction had a measurable rate around 50° and therefore the present kinetic study was carried out at 50° unless otherwise specified. The oxidation products, CO_2 and NH_3 were identified by their characteristic spot test[9]. CO_2 was identified by using conventional baryta water test. The presence of NH_3 was tested with Nesseler's reagent.

The stoichiometry of the reaction was determined taking excess of bromate over the $[HCONH_2]$ along with acid and mercuric acetate and kept for 24 h. The excess bromate was estimated iodometrically. These studies indicate that 3 moles of amide are consumed for 1 mole of bromate,

$$3HCONH_2 + BrO_3^- \xrightarrow[H_2O]{H^+} 3CO_2 + 3NH_3 + Br^- \tag{4}$$
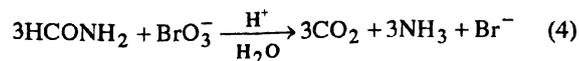
The above stoichiometry was also verified by the mole-ratio method in which bromate was taken in excess compared to [amide] along with fixed concentrations of acid and mercuric acetate. The reactions were performed under nitrogen atmosphere for ~24 h at suitable temperature along with a blank. Aliquot (5 ml) of the reaction mixture was drawn at suitable intervals of time and the unreacted [bromate] was estimated. log $[BrO_3^-]_t$ was plotted against time. The curve consisted of two portions, the first portion for the oxidation of substrate with a definite slope and the second parallel to blank run. The intersecting point is equal to the concentration of bromate consumed for the substrate. From the intersecting point, the stoichiometry was calculated to be 3 moles of amide to 1 mole of BrO_3^-.

Acknowledgement

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