Kinetics & Mechanism of the Oxidation of N-Methylformamide by Aquothallium(III) in Perchloric Acid Media

K S GUPTA
Department of Chemistry, University of Rajasthan, Jaipur 302 004

and

S D SAXENA
Department of Chemistry, D A V College, Kanpur

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Kinetics of oxidation of N-methylformamide (NMF) by thallium(III) is studied in perchloric acid medium and the results are compared with the oxidation of formamide and dimethylformamide. When initial [HClO₄] > [NMF], actual reducing agent is formic acid whereas if initial [NMF] > [HClO₄], both HCOOH and unhydrolysed NMF act as reducing agents. The reactivity sequence, formamide > NMF > dimethylformamide fits the Taft structure-reactivity correlation which yields a value of $-1.2 \pm 0.05$ for reaction constant, $\rho$, showing the amide oxidation to be strongly influenced by polar effects.

Recently we reported the kinetics of the oxidation of formamide¹ and dimethylformamide² by thallium(III) and found that the oxidation of formamide differed from that of DMF. Literature survey revealed that the kinetics of the oxidation of N-methylformamide (NMF) by Tl(III) has not been studied previously with any oxidant and hence the need for the title investigation. Only recently Ahmed and coworkers³ have studied the oxidation of NMF and formamide under the condition $[\text{Amide}] < [\text{HClO}_4]$ (subscript i refers to initial concentration) where these amides are actually present as formic acid due to their rapid hydrolysis. Thus their results³ pertain to the oxidation of formic acid rather than NMF¹⁻³.

N-Methylformamide was a Fluka(purum) product. All other chemicals and procedure for following the kinetics by determining thallium(III) iodometrically. The product CH₃NH₃ was not oxidised. Similar results have been obtained by other workers also³.

In the situation $[\text{HClO}_4] > [\text{NMF}]$, the actual reductant is formic acid¹⁻³. The experiments were performed under pseudo order conditions by keeping [NMF] in excess. The pseudo-first order rate constants, $k_{obs}$ for the variation of Tl(III) in the range $5 \times 10^{-3}$ to $1 \times 10^{-2} M$ and [NMF], in the range $4 \times 10^{-2}$ to $0.01 M$ were in agreement with the rate law¹⁻²

$$\text{Rate} = k_{obs} = \frac{k_1 K_1 [\text{NMF}]_i}{1 + K_1 [\text{NMF}]_i}$$

where $K_1$ is the equilibrium constant of the reaction

$$\text{HCOOH} + \text{Tl}^{III} \rightarrow \text{CO}_2 + \text{H}_3\text{NH}_3 + \text{H}^+$$

(1)

and $k_1$ is the rate constant of the rate-determining step

$$\text{[HCOOHTl]}^3+ \rightarrow \text{HCOOH} + \text{CO}_2 + 2\text{H}^+$$

(3)

The values of $k_1$ and $K_1$ were found to be $1.0 \pm 0.1 \times 10^{-4} \text{dm}^3 \text{mol}^{-1} \text{s}^{-1}$ and $19 \pm 1 \text{dm}^3 \text{mol}^{-1}$ respectively at $70^\circ$.

The variation in $[\text{HClO}_4]$, (1-2M) did not influence the rate as pointed out earlier¹⁻³⁻⁹.

In the range $[\text{NMF}] > [\text{HClO}_4]$, in all the experiments the initial concentrations of NMF and HClO₄ were so adjusted that the concentration of the unhydrolysed amide, [NMF], was always in excess over thallium(III). Under this condition the concentration of unhydrolysed amide, [NMF] is given¹⁻² by the relation, $[\text{NMF}] = [\text{NMF}]_i - [\text{HClO}_4]_i$. Thus [NMF] was varied from 1.84 to
4.68 M at a fixed [HClO₄] = 1.1 M at 70° to give an effective variation in [NMF] from 0.74 to 3.59 M. In this situation the kinetics followed a pseudo-first order course. The values of $k_{obs}$ (see Table 1) for all these variations obeyed the two term rate law (5)

$$k_{obs} = k_1 + k_2 [\text{NMF}]$$

In accordance with the rate law (5) the plots of $k_{obs}$ versus [NMF] were linear. The values of $10^4 k_1$ and $10^5 k_2$ obtained from these plots at 65, 70 and 75° are 0.66, 1.1, 1.75 and 0.5, 0.8 and 1.32 dm$^3$ mol$^{-1}$ s$^{-1}$ respectively.

The increase in [HClO₄], from 1.1 to 2.9 M at constant [NMF] = 3.42 M and [Tl(III)] = 5 x 10$^{-3}$ M at 75° decreased the rate. This is due to the fact that at higher [HClO₄], there is decrease in the concentration of unhydrolysed NMF, as reported earlier. The variation of ionic strength from 1 to 3 M (LiClO₄) did not influence the rate of oxidation.

From the values of $k_2$ determined at 65, 70 and 75°, the values of $\Delta H^\circ_2$ and $\Delta S^\circ_2$ were calculated to be $108 \pm 4$ kJ mol$^{-1}$ and $-5.85 \pm 1.25$ JK$^{-1}$ mol$^{-1}$ respectively.

The oxidations of formamide, dimethylformamide and N-methylformamide follow essentially the same kinetics under the condition [HClO₄] > [amide], and the reaction is primarily the oxidation of formic acid. Looking to the fact that the starting material in each case was different the agreement in $k_1$ and $K_1$ values for different amides and formic acid is good (Table 2).

However, under the condition [amide], > [HClO₄], the kinetic results for both NMF and DMF$^2$ are similar. In both the cases, the disappearance of thallium(III) follows a first order course. On the contrary in the case of formamide under similar conditions the disappearance of thallium(III) follows a zero order kinetics, yet the concentration order in [Tl(III)] is one. It is therefore, from the values of $k_2$ determined at 65, 70 and 75°, the values of $\Delta H^\circ_2$ and $\Delta S^\circ_2$ were calculated to be $108 \pm 4$ kJ mol$^{-1}$ and $-5.85 \pm 1.25$ JK$^{-1}$ mol$^{-1}$ respectively.

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Table 1 -- Values of $k_{obs}$ for the Variation of [NMF], [Tl(III)], and [HClO₄], at $\mu = 1.1$ M

<table>
<thead>
<tr>
<th>Temp. = 65°</th>
<th>[NMF] [mol dm$^{-3}$]</th>
<th>[HClO₄] [mol dm$^{-3}$]</th>
<th>[Tl(III)] [mol dm$^{-3}$]</th>
<th>$k_{obs}$ [s$^{-1}$]</th>
</tr>
</thead>
<tbody>
<tr>
<td>5.00</td>
<td>3.05</td>
<td>1.10</td>
<td>1.95</td>
<td>1.1</td>
</tr>
<tr>
<td>5.00</td>
<td>3.80</td>
<td>1.10</td>
<td>2.70</td>
<td>1.1</td>
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<tr>
<td>5.00</td>
<td>4.75</td>
<td>1.10</td>
<td>3.65</td>
<td>1.1</td>
</tr>
<tr>
<td>5.00</td>
<td>5.13</td>
<td>1.10</td>
<td>4.05</td>
<td>1.1</td>
</tr>
<tr>
<td>Temp. = 70</td>
<td>1.00</td>
<td>1.84</td>
<td>1.10</td>
<td>0.74</td>
</tr>
<tr>
<td>3.00</td>
<td>1.84</td>
<td>1.10</td>
<td>0.74</td>
<td>1.1</td>
</tr>
<tr>
<td>5.00</td>
<td>1.84</td>
<td>1.10</td>
<td>0.74</td>
<td>1.1</td>
</tr>
<tr>
<td>7.00</td>
<td>1.84</td>
<td>1.10</td>
<td>0.74</td>
<td>1.1</td>
</tr>
<tr>
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<td>2.70</td>
<td>1.10</td>
<td>1.60</td>
<td>1.1</td>
</tr>
<tr>
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<td>1.85</td>
<td>1.1</td>
</tr>
<tr>
<td>5.00</td>
<td>3.76</td>
<td>1.10</td>
<td>2.66</td>
<td>1.1</td>
</tr>
<tr>
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<td>4.68</td>
<td>1.10</td>
<td>3.58</td>
<td>1.1</td>
</tr>
<tr>
<td>Temp. = 75</td>
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<td>1.71</td>
<td>1.10</td>
<td>0.61</td>
</tr>
<tr>
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<td>1.10</td>
<td>1.46</td>
<td>1.1</td>
</tr>
<tr>
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<td>2.32</td>
<td>1.1</td>
</tr>
<tr>
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<td>3.55</td>
<td>1.10</td>
<td>2.45</td>
<td>1.1</td>
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<tr>
<td>5.00</td>
<td>3.42</td>
<td>1.66</td>
<td>1.76</td>
<td>1.1</td>
</tr>
<tr>
<td>5.00</td>
<td>3.42</td>
<td>2.90</td>
<td>0.52</td>
<td>2.9</td>
</tr>
</tbody>
</table>

(a) ionic strength was 3.0 M adjusted with lithium perchlorate. (b) In the situation [NMF] > [HClO₄], [HCOOH] = [HClO₄], (see reference 1).

Table 2 -- Rate Parameters for the Oxidation of Formamide, NMF, DMF and HCOOH at 70° and $\mu = 1.1$ M

<table>
<thead>
<tr>
<th>Rate parameters</th>
<th>HCONH₂</th>
<th>NMF</th>
<th>DMF</th>
<th>HCOOH</th>
<th>H₂O</th>
</tr>
</thead>
<tbody>
<tr>
<td>$10^6 k_1$, dm$^3$ mol$^{-1}$ s$^{-1}$</td>
<td>1.2 ± 0.1$^a$</td>
<td>1.1 ± 0.1$^b$</td>
<td>0.87 ± 0.1$^a$</td>
<td>1.3$^c$</td>
<td>—</td>
</tr>
<tr>
<td>$K_1$, dm$^3$ mol$^{-1}$</td>
<td>15 ± 1$^a$</td>
<td>19 ± 1$^b$</td>
<td>15 ± 1$^c$</td>
<td>16$^c$</td>
<td>—</td>
</tr>
<tr>
<td>$10^6 k_2$, dm$^3$ mol$^{-1}$ s$^{-1}$</td>
<td>4.3 ± 0.2$^a$</td>
<td>0.8 ± 0.05$^b$</td>
<td>0.55 ± 0.5$^c$</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>$K_2$, dm$^3$ mol$^{-1}$</td>
<td>7.2 ± 0.04$^a$</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>$pK_a$</td>
<td>-2.0$^a$</td>
<td>-1.52$^b$</td>
<td>-1.33$^c$</td>
<td>—</td>
<td>-1.7$^c$</td>
</tr>
</tbody>
</table>

(a) reference (1); (b) this work; (c) reference (2); (d) calculated using $\Delta H_f^\circ = 108.8$ kJ mol$^{-1}$ and $k = 1.7 \times 10^{-4}$ dm$^3$ mol$^{-1}$ s$^{-1}$ at 74° given in ref. (12); (e) reference (12); (f) reference (13); (g) reference (14).
difficult to visualise how the substitution of one or two methyl groups at nitrogen in HCONH₂ changes the course of the kinetics although the fundamental rate law for all the three amides is the same. The results of this study too are explainable in terms of the general mechanism (see Eqs 1-4 of references 1 and 2) which leads to the rate law (6)

\[
\frac{k_1 K_1 [\text{HCOOH}] + k_2 K_2 [\text{HCOOH}]}{[\text{NMF}] + k_3 K_3 [\text{NMF}]} = k_{\text{obs}} \tag{6}
\]

where \( K_2 \) and \( K_3 \) are equilibrium constants for the formation of \([\text{TI(HCOOH)(NMF)}]^{3+}\) and \([\text{TI(NMF)}]^{3+}\) complexes respectively from \([\text{TI(HCOOH)}]^{3+}\) and NMF and \([\text{TI(NMF)}]^{3+}\) and NMF. \( k_2 \) and \( k_3 \) are respective rate constants for the decomposition of these complexes. Since the kinetics does not indicate a complex formation between Ti(III) and NMF, the values of \( K_2 \) and \( k_3 \) should be much smaller as compared to \( K_1 \), i.e.,

\[
1 + K_1 [\text{HCOOH}] \gg (K_1 K_2 [\text{HCOOH}] + K_2) [\text{NMF}] \Rightarrow k_1 K_1 > k_3 K_3 \ll k_2 K_1 K_2 \quad \text{holds} \quad \text{and the rate law (6) will reduce to (7)}
\]

\[
k_{\text{obs}} = \frac{k_1 K_1 + k_2 K_2 [\text{NMF}][\text{HCOOH}]}{1 + K_1 [\text{HCOOH}]} \tag{7}
\]

Since under our experimental conditions, \( K_1 [\text{HCOOH}] \gg 1 \), Eq. (7) simplifies to Eq. (8).

\[
k_{\text{obs}} = k_1 + k_2 K_2 [\text{NMF}] \tag{8}
\]

which is same as Eq. (5) with \( k_2' = k_2 K_2 \). A comparison of the values of \( k_2' \) for DMF and NMF with \( k_2 K_2 \) for formamide and \( k_1 K_1 \) for formic acid leads to the reactivity sequence, \( \text{HCOOH} > \text{HCONH}_2 \) > \( \text{HCONHCH}_3 \) > \( \text{HCON(CH}_3)_2 \) which can be explained on the basis of combined inductive and mesomeric effects\(^{1,10}\).

The \( k_2' \) values correlate very well with polar substituent constants, \( \sigma \), for N-alkyl substituents in terms of the Taft equation\(^{11}\). The \( \sigma \) values of zero, 0.57 and 0.76 for substituents NH₂, –NHCH₃ and –N(CH₃)₂ obtained by Yamana and co-workers\(^8\) respectively were used. The plot of \( \log k \) versus \( \sigma \) was linear, yielding a \( p \)-value of \( -1.2 \pm 0.05 \), indicating that the oxidation of N-alkylated formamides is greatly susceptible to polar effects.

References