Kinetics of Chromic Acid Oxidation of Hydroxylamine & Nitrous Acid

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Oxidations of hydroxylamine and nitrous acid with chromic acid have been found to be of second order, first order each with respect to [Cr(VI)] and [substrate]. The effects of hydrogen ion, manganous ion and pyridine concentrations on the rates have been studied. The energy (ΔE) and entropy (ΔS) of activations have been evaluated to be 8·4 (kcal mol⁻¹), -25·3 (cal deg⁻¹ mole⁻¹) and 7·5 (kcal mol⁻¹), -39·0 (cal deg⁻¹ mole⁻¹) for the oxidation of hydroxylamine and nitrous acid, respectively. Hydroxylamine is oxidized to nitrous acid. Further oxidation of nitrous acid is too slow to be studied under the conditions in which hydroxylamine is oxidized. However, the chromic acid oxidation of nitrous acid is significant at [H⁺]>10⁻³M.

Materials and Methods

All the chemicals used were of analar (BDH) or GR (E. Merck) grade. A stock solution (10⁻²M) of hydroxylamine hydrochloride was prepared and estimated bromatometrically. Sodium acetate-acetic acid (pH 4·5) was used for the oxidation of hydroxylamine. Nitrite ion was added as sodium nitrite while [H⁺] was varied by the addition of HClO₄. D₂O was supplied by BARC, Bombay and is claimed to have a deuterium content of 99·4%.

Kinetic measurements — All kinetic runs with hydroxylamine were followed by measuring the decrease in absorbance at 355 nm using cells of 1 cm path-length in a Beckman DU model spectrophotometer as described earlier. For the other reaction, Cr(VI) absorbance was measured at 400 nm (not at the absorption maximum) in order to minimize spectral interference from nitrite. All the reactants, except Cr(VI) and products, have negligible absorption at this wavelength. The reactions were followed up to 90% reduction of initial oxidant and generally 6-8 experimental points were taken in each run. The pseudo first order rate constant (kobs) was determined from the gradient of log OD (optical density) versus time plot, and was reproducible to ±5%.

Results

Stoichiometry and product analysis — The stoichiometry was determined by estimating the excess of hydroxylamine. The mole consumption ratio [Cr(VI)]/[NH₃OH⁺] was found to be 1·33, 1·30 and 1·41 at pH 4·5, 4·7 and 4·98, respectively. The average of these determinations is 1·34, which indicates that hydroxylamine is oxidized to nitrous acid. The UV spectrum of oxidation product was recorded in the region 220-380 nm using a quartz cell of pathlength 10 cm and showed no absorption maximum at 301 nm indicating that nitrate ion is absent. On the other hand, the spectrum showed a strong absorption maximum at 355 nm where the nitrite ion has an absorption maximum (ε = 25 M⁻¹ cm⁻¹). The absorption maximum (ε = 25 M⁻¹ cm⁻¹) and pH = 6·04, whereas kobs for the other reaction was (3·30 ± 0·05) × 10⁻²M sec⁻¹ at 20° and [Cr(VI)] = (4·15-7·5) × 10⁻³M and [H⁺] = 6·04, whereas kobs for the other reaction was (3·30 ± 0·05) × 10⁻²M sec⁻¹ at 20° and [Cr(VI)] = (4·15-7·5) × 10⁻³M and [H⁺] = 6·04.

Effect of varying [reactant] — The first order rate constants were calculated at various initial [Cr(VI)] but at constant [substrate], acidity and pH = 1·0 M (NaClO₄). The average value of kobs was (1·55 ± 0·02) × 10⁻² sec⁻¹ at 10° and [Cr(VI)] = (4·15-7·5) × 10⁻³M, [NH₃OH⁺] = 3·0 × 10⁻²M and pH = 6·04.

In another set of experiments first order rate constants were measured at different [substrate] but at constant [Cr(VI)] and pH. Plots of [1/kobs] versus [1/substrate] at different temperatures were linear (Fig. 1).

Effect of varying pH — The value of kobs increased with increasing [H⁺] (Table 1). The plots of log
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Table 1 - Effect of Varying pH on the Pseudo First Order Rate Constants (kobs)

| pH  | kobs x 10^4 (sec^-1) | kobs x 10^4 | kobs/|H^+| x 10^2 (litre mole^-1 sec^-1) |
|-----|----------------------|-------------|------|--------------------------------|
| 5.18| 3.70                 | 1.0         | 9.98 | 0.998                          |
| 5.48| 3.37                 | 1.30        | 4.92 | 0.984                          |
| 5.60| 3.07                 | 1.46        | 3.78 | 1.06                           |
| 5.90| 2.34                 | 1.60        | 2.97 | 1.18                           |
| 6.04| 1.54                 | 1.82        | 1.72 | 1.13                           |
| -   | -                    | 2.00        | 1.08 | 1.08                           |

kobs versus pH were linear with slope value less than unity (0.45) for the reaction with hydroxylamine, and unity for the reaction with HNO₂. This suggests that kobs is directly proportional to [H⁺] in the case of reaction with HNO₂. The quotients, kobs/[H⁺] for this reaction are given in Table 1.

Effect of added Mn(II) ions - Mn(II) is generally known to retard9,10 the rate of oxidation of organic and inorganic substrates by Cr(VI) but in some cases, it has been found to accelerate11,12 the rate of oxidation. In the present study Mn(II) has been found to retard the rate of oxidation of hydroxylamine (Table 2). The retardation may be considered mainly due to the change in [Mn(II)] and not due to the change in ionic strength since the addition of NaClO₄ or NaCl (1-0 x 10⁻⁶, 10⁻²M) to the reaction mixture does not seem to have any influence on the reaction rate. However, at [Mn(II)] ≥ 8.0 x 10⁻²M, kobs decreased by 50% of that obtained in the absence of Mn(II). This is expected if Mn(U) catalyses the disproportionation of intermediate valency-states of chromium13. This further suggests that Cr(IV) is probably involved as intermediate. Retardation by Mn(U) may also be explained by assuming that Cr(VI) forms an intermediate complex with the substrate which may decompose to give the products, while Mn(U) forms an unreactive complex with the substrate. On the other hand, the value of kobs was found to increase linearly with increasing [Mn(U)] in the reaction with HNO₂ although the increase was not very significant (Table 2). This may be due to complications arising from a reaction of Mn(U) with HNO₂.

Effect of added pyridine - Addition of pyridine does not seem to have any influence on the rate of oxidation of hydroxylamine as pointed out earlier10,13 However, the pseudo first order rate constant decreases considerably with increasing [pyridine] for the nitrite reaction. Since the ionization constant14 of pyridinium ion is very small (4.0 x 10⁻⁶ at 35°C) compared to [HClO₄] (5.0 x 10⁻⁵M), the concentration of free pyridine in the solution is bound to be very small for the nitrite reaction. The results indicate that pyridine does not catalyze the oxidation of nitrous acid (Table 3).

Effect of temperature and thermodynamic parameters - The second order rate constants (k₂) were calculated from the relation, k₂ = kobs/[substrate]. The average values of k₂, calculated from several determinations were 6.2, 8.1, 9.8 and 12.8 (litre mole⁻¹ sec⁻¹) at 11.5°C, 16.5°C, 21.5°C and 26°C respectively for the oxidation of hydroxylamine and 6.55 x 10⁻², 7.30 x 10⁻², 9.1 x 10⁻² and 12.55 x 10⁻² litre mole⁻¹ sec⁻¹ at 27°C, 32°C, 37°C and 42°C, respectively for the nitrite oxidation. The energy (ΔE) and entropy (ΔS) of activations were computed as described earlier15. The activation parameters obtained for the chromic acid oxidations of some

Fig. 1 — Plots of 1/kobs versus 1/[substrate] at different temperatures (a): [Chromium(VI)] = 4.16 x 10⁻⁵M; pH = 6.04; (b): [Chromium(VI)] = 3.33 x 10⁻⁴M; pH = 1.30

Table 2 — Effect of Added Mn(II) Ions on kobs

<table>
<thead>
<tr>
<th>[Mn(II)] x 10⁻² M</th>
<th>kobs x 10⁴ sec⁻¹</th>
<th>[Mn(II)] x 10⁻² M</th>
<th>kobs x 10⁴ sec⁻¹</th>
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</thead>
<tbody>
<tr>
<td>0.0</td>
<td>1.54</td>
<td>0.0</td>
<td>3.35</td>
</tr>
<tr>
<td>2.0</td>
<td>1.28</td>
<td>1.0</td>
<td>3.54</td>
</tr>
<tr>
<td>4.0</td>
<td>1.15</td>
<td>2.0</td>
<td>3.73</td>
</tr>
<tr>
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<td>3.0</td>
<td>4.03</td>
</tr>
<tr>
<td>8.0</td>
<td>0.77</td>
<td>5.0</td>
<td>4.22</td>
</tr>
</tbody>
</table>

10.0
reducing nitrogen, phosphorus and arsenic compounds are recorded in Table 4. The values obtained in the present studies are not widely different (except phosphorous acid) from those for other reductants, suggesting that similar mechanisms may also be operating in the oxidation of hydroxylamine and nitrite ion.

**Solvent isotope effect** — The rates of oxidation were measured both in H₂O and D₂O. The ratios k₃₀/k₅₀ were calculated to be 0·8 at 10° and 1·8 at 20° for the oxidations of hydroxylamine and nitrous acid, respectively (condition same as in Table 2). The latter ratio is quite close to the solvent isotope effect (k₃₀/k₅₀ = 2·2-2·5) expected for proton-catalysed reactions. This solvent isotope effect would favour all reactions involving molecular chromic acid, because equilibrium (1) is shifted by D₂O in the forward direction thereby yielding higher [H₃CrO₄] than what could be present in water.

\[
\text{HCrO}_3 + \text{H}_2\text{O}^+ \rightleftharpoons \text{H}_2\text{CrO}_4 + \text{H}_2\text{O} \quad \text{(1)}
\]

The value (0·8) of solvent isotope effect obtained for the oxidation of hydroxylamine further suggests that HCrO₃ and not H₂CrO₄ is the reactive oxidant in the oxidation of hydroxylamine.

**Discussion**

The kinetics of oxidation of hydroxylamine may be explained by either of the following steps:

\[\text{NH}_2\text{OH}^+ + \text{HCrO}_4 \rightleftharpoons \text{complex} \rightarrow \text{products of reaction} \quad \text{(2)}\]

\[\text{NH}_2\text{OH}^+ + \text{HCrO}_4 \rightleftharpoons \text{complex} \rightarrow \text{products of reaction} \quad \text{(3)}\]

The plots of 1/k₉₀ versus 1/[NH₂OH⁺] at different temperatures (Fig. 1) indicate that intermediate compound formation is unlikely. If K is small in step (2), it would give second order kinetics consistent with complex formation. We conclude that the reaction takes place through step (3). Gutch and Waters showed that hydroxylamine can be oxidized to short-lived free radicals by one-electron abstracting oxidants. In the present investigation, however, the addition of acrylamide to the reaction mixture failed to give any cloudy suspension indicating that free radicals are not formed in solution and Cr(VI) appears to behave as a two equivalent oxidant in the oxidation of hydroxylamine. However, the electron transfer takes place through protonation of the oxicle-ligand on Cr(VI) and finally deprotonation of H₂N⁺ so as to allow migration of an electron pair to Cr(VI) through the π-system of the bridging O giving the intermediate complex (X) which finally decomposes to give HNO and Cr(IV) as shown in Eq. (4).

\[
\text{H}^+ + \text{HNO} + \text{Cr(IV)} \rightarrow \text{H}_2\text{O} + \text{NO} + \text{Cr}_2\text{O}_7^\text{2-} \quad \text{(4)}
\]

It is known that a two-electron reducing agent such as Sn(II) reacts with HNO₂ to form an unstable intermediate called nitrosyl (HNO). Bray et al. studied the oxidation of hydroxylamine by Fe(III) and showed that Fe(III) ion does not oxidize HNO to HNO₂. However, a more powerful oxidizing agent than Fe(III) oxidizes hydroxylamine to HNO₂. The redox potentials of Cr(VI) +3e⁻→Cr(III) and Cr(IV) +2e⁻→Cr(III) couples are 1·36 and 1·75 V, respectively. Consequently, both Cr(VI) and Cr(IV) are more powerful oxidants than Fe(III) and are capable of oxidizing HNO to HNO₂. Cr(IV) which is generated in step (4) may disproportionate to give Cr(V) and Cr(III) or react rapidly with Cr(VI) to give Cr(V). The latter finally oxidizes HNO to HNO₂. Rocek et al. have shown that Cr(IV) also reacts with some organic compounds. The addition of acrylamide to the reaction mixture failed to give any cloudy suspension indicating further that Cr(IV) does not react with NH₂OH⁺. It has earlier been reported that NH₂O radicals dimerize to give N₂. No formation of nitrogen gas in the present study further supports the above contention. The values of k₉ were determined at different temperatures for both the reactions. The extrapolated values of k₉ at 25° for the oxidations of hydroxylamine (at pH 6·04) and nitrous acid (at...
the present work may look more plausible and justify
found a nonlinear dependence on [RN02+] and that
they obtained a plot which had a positive intercept
1'3) are 11·5 and 5·6×10⁻⁴ (litre mole⁻¹ sec⁻¹),
respectively. The second order rate constant
for the oxidation of HNO₂ at pH 6·04 would be 1·02
×10⁻⁴ litre mole⁻¹ sec⁻¹. This suggests that further
oxidation of HNO₂ is too slow under the conditions
in which hydroxylamine is oxidized. Again, the
dissociation constant of RN0₂ is 4·5× 10⁻⁴, and this
will remain undissociated in the presence of [R⁺]
6·04 would be 1·02
10⁻⁶ litre mole⁻¹ seel. This suggests that further
the postulated steps (5 and 6) in Scheme 1 and steps
(11 and 12) in Scheme 2. It has earlier been pointed
out that disproportionation of Cr(IV) actually takes
place in chromic acid oxidations and that Cr(VI)
oxidation of Cr(IV) is ruled out. It is likely, there­
fore, that the oxidation of HNO₂ takes place
following the steps suggested in Scheme 2.

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