Outer-sphere mechanism of oxidation of hydrazine and hydrazinium ion by 12-tungstocobaltate(III) ion in acetate-acetic acid buffer: Marcus treatment

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Oxidation of hydrazine by 12-tungstocobaltate(III) in acetate buffer is expressed by the following equation in view of the stoichiometric ratio \( \Delta[\text{Co(III)W}^5\text{+}] / \Delta[\text{hydrazine}] = 4.05 \pm 0.09 \).

\[
4[\text{Co(III)W}^5\text{+}] + \text{N}_2\text{H}_4 \rightarrow 4[\text{Co(II)W}^6\text{+}] + \text{N}_2 + 4\text{H}^+
\]

The spectral studies of the reaction mixture at \( \text{pH} \leq 2 \) indicate that the absorbancy of the reaction mixture is more than that of \([\text{Co}^{II}\text{W}^5\text{+}]\) ion and less than the \([\text{Co}^{II}\text{W}^5\text{+}]\) ion at \( \text{pH} > 2 \). This is attributed to the equilibrium between \( \text{N}_2\text{H}_4 \) and \( \text{N}_2\text{H}_4^+ \) and that both of these species are reactive. Oxidation of \( \text{N}_2\text{H}_4 \) is at least \( 10^4 \) times faster than the oxidation of \( \text{N}_2\text{H}_4^+ \) ion. This is attributed to the availability of two lone pairs of electrons on nitrogen atoms in \( \text{N}_2\text{H}_4 \). In \( \text{N}_2\text{H}_4^+ \) one of the lone pairs is polarised towards the nitrogen bearing the proton and is thus not easily available for coordination. The dependence of rate on \( [\text{H}^+] \) is given by the expression \( k_2 = (k + k, K [\text{H}^+]^n) \) where \( k_2 = k\text{ob}/4[\text{hydrazine}] \) and \( k \) and \( k, \) are the composite rate constants. The reaction is considered outer-sphere in nature and the same is supported by the application of Marcus theory.

Oxidation of hydrazine has attracted attention, perhaps, because its oxidation products differ with one and two electron equivalent oxidants\(^1\).\(^2\). The oxidation of nitrogen compounds by 12-tungstocobaltate(III) ion, \([\text{Co}^{II}\text{O}_4\text{(WO)}_{12}]^\text{3-}\) hereafter represented as \([\text{Co}^{II}\text{W}^5\text{+}]\), has received little attention. We recently investigated the oxidation of hydroxylamine\(^3\) and found that \( \text{NH}_2\text{OH} \) and not \( \text{NH}_2\text{OH}^+ \) formed an intermediate complex with \([\text{Co}^{III}\text{W}^5\text{+}]\) which disproportionate into the products. It was surprising because the positive charge on \( \text{NH}_2\text{OH}^+ \) made it the most appropriate species to react with the negatively charged \([\text{Co}^{III}\text{W}^5\text{+}]\) ion. The inactivity of \( \text{NH}_2\text{OH}^+ \) is traced to the lack of availability of a lone pair of electron on nitrogen atom needed for coordination. It was, therefore, considered appropriate to investigate another similar compound to confirm whether the availability of the pair of electrons on nitrogen atom is essential.

Materials and Methods

12-Tungstocobaltate(III) was prepared as described earlier\(^4\). The sample had maximum absorbancy at 388 nm against the value 390 nm reported in the literature\(^5\). Buffer solutions of desired \( \text{pH} \) were prepared from sodium acetate and acetic acid as described elsewhere\(^6\). Hydrazine perchlorate was prepared by mixing equivalent amounts of hydrazine hydrate (Loba-Chemie, LR) and perchloric acid (E Merck, GR) and analysed by bromate titration\(^7\). Other chemicals were either AnalyR or GR grade. The solutions, prepared in doubly distilled water, were standardised by standard titrimetric methods. Doubly distilled water was used throughout.

Rate measurements

The preliminary investigations indicated that the rate was unaffected when atmospheric oxygen was replaced with nitrogen gas. Hence, no efforts were made to exclude air from the reaction mixture. The kinetics was studied in acetate-acetic acid buffer (\( \text{pH} \) 4.27) at constant ionic strength (\( \mu = 0.4 \text{ mol dm}^{-3}, \text{NaClO}_4 \)) under pseudo-first order conditions ([Co(III)W]\(^5\text{+} \approx [\text{hydrazine}]\) by monitoring the optical density of [Co(III)W]\(^5\text{+}\) ion at 390 nm using a Photoelectric Instruments SFA-11 colorimeter based on the stopped-flow method. The optical density at infinite time, \( A_{\infty} \), was always measured after 20-24 h after the
initiation of the reaction. Hydrazine is transparent at 390 nm. The pseudo first order rate constant \( k_{\text{obs}} \) is evaluated from the plots of \( \log(A_t - A_0) \) against time using a computer program and its values from replicate runs agreed to within ±5%. The plots are linear for more than two half-lives of the reaction indicating that reaction products do not interfere with the rate profile. Rates measured at 620 nm (appearance of \([\text{Co}^{II}W]^{6-}\)) yielded similar \( k_{\text{obs}} \) values.

Addition of freshly distilled acrylonitrile (1 ml) to the reaction mixture, purged with nitrogen, resulted in the formation of polyacrylonitrile indicating the presence of free radical. The monomer was not polymerised by the blank solutions of hydrazine and \([\text{Co}^{III}W]^{5+}\) ion.

**Stoichiometry**

A number of reaction mixtures with different initial concentrations of \([\text{Co}^{II}W]^{5+}\) and [hydrazine] \(([\text{Co}^{III}W]^{5+} >> [\text{Hydrazine}]\)) were prepared in solutions of differing pH. The average ratio of \( \Delta[\text{Co}^{III}W]^{5+} / \Delta[\text{hydrazine}] \), based on the estimation of unreacted \([\text{Co}^{III}W]^{5+}\) at 390 nm at the end of the reaction was 4.05 ± 0.09. The stoichiometry of 4:1 is expressed by Eq. (1).

\[
4[\text{Co}^{III}W]^{5+} + \text{N}_2\text{H}_4 \rightarrow 4[\text{Co}^{II}W]^{5+} + \text{N}_2 + 4\text{H}^+ \quad \text{(1)}
\]

**Spectral studies**

The spectral studies in the visible range were carried out on a HP 8452A spectrophotometer having a bandwidth of 2 nm. In Fig. 1 are shown the spectra of the reaction mixture \((10^4[\text{Co}^{III}W]^{5+} = 2.43, 10^4[\text{Hydrazine}] = 5.0 \text{ mol dm}^{-3} \) at 15°C) at \([\text{H}^+] = 0.09 \) (B) and 0.01 mol dm\(^{-3}\) (C) respectively. The spectra D and E are at pH 3.42 and 4.63 respectively. The spectrum A is that of \([\text{Co}^{III}W]^{5+}\) alone at \([\text{H}^+] = 0.09 \) mol dm\(^{-3}\).

**Results and Discussion**

**Dependence of \( k_{\text{obs}} \) on [Hydrazine]**

The dependence of \( k_{\text{obs}} \) on [Hydrazine] over a twentyfold variation in its initial concentration at pH 4.27 and constant ionic strength indicated a proportionate increase in the \( k_{\text{obs}} \) value. The passage of the linear plot between \( k_{\text{obs}} \) and [Hydrazine] through origin indicated a first-order dependence in hydrazine.

**Dependence of \( k_{\text{obs}} \) on pH**

The results of the effect of initial pH on the \( k_{\text{obs}} \), at different temperatures, Table 1, indicated that the rate
Table 1 — Dependence of \( k_1 (= k_{\text{obs}}/[\text{hydrazine}]) \) on pH at different temperatures. 
\[ 10^9[\text{Co}^{\text{III}}W^3^-] = 9.0, 10^9[\text{Hydrazine}] = 1.0 \text{ and } \mu = 0.56 \text{ mol dm}^{-3} \]

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Table 2 — Values of \( k \) and \( k_1 \) (dm³ mol⁻¹ sec⁻¹) and the associated activation parameters

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<td>( 10^{-4}(k/k) )</td>
<td>1.57</td>
<td>1.81</td>
<td>1.79</td>
<td>2.09</td>
<td>2.25</td>
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\[
\Delta H_r^\pm = 17 \pm 1 \text{ kJ mol}^{-1} \quad \Delta H_m^\pm = 31 \pm 1 \text{ kJ mol}^{-1} \\
\Delta S_r^\pm = -216 \pm 2 \text{ J K}^{-1} \text{ mol}^{-1} \quad \Delta S_m^\pm = -90 \pm 2 \text{ J K}^{-1} \text{ mol}^{-1}
\]

increased with the pH. The linear plots between \( k_2 \left(= k_{\text{obs}}/[\text{hydrazine}] \right) \) and \([\text{H}^+] \) having intercepts on the rate ordinate are consistent with the empirical relation (2).

\[
k_2 = a + b[\text{H}^+]^{-1} \quad \ldots(2)
\]

The \( k_{\text{obs}} \) value was independent of added [Co(II)W⁶⁺]. It indicated that the electron-transfer step is the one determining the reaction rate. The formation of an intermediate complex between hydrazine and \([\text{Co}^{\text{III}}W]^-\) ion is supported by the spectral studies of the reaction mixture. The results shown in Fig. 1 indicated the presence of different hydrazine species in the two range of \([\text{H}^+] \) ion (\( 2 \leq \text{pH} \leq 2 \)).

An equilibrium between \( \text{N}_2\text{H}_4^+ \) and \( \text{N}_2\text{H}_4 \); Eq. (3), is known and the dissociation constant \( K_1 = 8.7 \times 10^{-4} \text{ mol dm}^{-3} (\mu = 0.5 \text{ mol dm}^{-3}, 25^\circ \text{C} \) and \( \Delta H = 39.3 \text{ kJ mol}^{-1} ) \). In view of the equilibrium and in the light of the spectral results, it is suggested that for solutions 0.01 \( \ll [\text{H}^+] \) > 0.01 mol dm⁻³, the dominant species of hydrazine are \( \text{N}_2\text{H}_5^+ \) and \( \text{N}_2\text{H}_3 \), respectively. That both species are simultaneously reactive is indicated by the empirical Eq. (2) describing the dependence of \( k_2 \) on the initial \([\text{H}^+] \). With these assumptions the most probable mechanism of the reaction is postulated as given by reactions (3)-(10).

\[
\begin{align*}
K_1 & : \text{N}_2\text{H}_4^+ \rightleftharpoons \text{N}_2\text{H}_4 + \text{H}^+ \\
K_2 & : \text{[Co}^{\text{III}}\text{W}]^+ + \text{N}_2\text{H}_4^- \rightleftharpoons \text{[Co}^{\text{III}}\text{W}^-\text{N}_2\text{H}_4]^+ \\
K_3 & : \text{[Co}^{\text{III}}\text{W}]^+ + \text{N}_2\text{H}_4^- \rightleftharpoons \text{[Co}^{\text{III}}\text{W}^-\text{N}_2\text{H}_4]^+ \\
K_4 & : \text{[Co}^{\text{III}}\text{W}^-\text{N}_2\text{H}_4]^+ \rightarrow \text{[Co}^{\text{III}}\text{W}]^+ + \text{N}_2\text{H}_4^- + \text{H}^+ 
\end{align*}
\]
Hydrazinium radical cation, $\text{N}_2\text{H}_5^+$, has been identified and characterised in aqueous solutions by pulse radiolysis. Its presence was qualitatively detected in the present case by the induced polymerisation of acrylonitrile. It appears that the radical cation disproportionates immediately into the hydrazyl radical ($\text{N}_2\text{H}_4^+$) and $\text{H}^+$. The hydrazyl radical can either dimerise or undergo dismutation to give diazine.

Further, diazine suffers rapid oxidation to $\text{N}_2$, as shown in Eq. (10). The above sequence of reactions are considered to account for the stoichiometry of the reaction requiring 4 moles of [Co(III)W] per mole of hydrazine. The rate law based on reactions (3) to (10) is expressed by equation (12). Since the reaction has a first order dependence in $[\text{N}_2\text{H}_5]$, the total [hydrazine], it is apparent that $([\text{H}^+] + K_s)^2 = (K_s[H^+] + K_{ka})[\text{N}_2\text{H}_5]$. In view of the value of $K_s$, it is assumed that $[\text{H}^+] = K_s$, Eq. (12) is reduced to Eq. (13) which is identical with the empirical rate law in Eq. (2).

\[ k_s [\text{Co}^{III}W \cdots \text{N}_2\text{H}_5] \rightarrow [\text{Co}^{III}W] + \text{N}_2\text{H}_4^+ \]  \hspace{1cm} (7)

\[ \text{N}_2\text{H}_4^+ \rightarrow \text{N}_2\text{H}_3 + \text{H}^+ \]  \hspace{1cm} (8)

\[ \text{N}_2\text{H}_3 + [\text{Co}^{III}W] \rightarrow \text{N}_2\text{H}_2 + [\text{Co}^{III}W]^+ + \text{H}^+ \]  \hspace{1cm} (9)

\[ \text{N}_2\text{H}_2 + 2[\text{Co}^{III}W] \rightarrow \text{N}_2 + 2[\text{Co}^{III}W] + 2\text{H}^+ \]  \hspace{1cm} (10)

Equation (13) is consistent with the linearity of the plots of $k_2$ versus $[\text{H}^+]$. The values of $k$ and $k_s$, at various temperatures, calculated from the intercepts and slopes of the plots are given in Table 2. It is interesting to note that the $k_s$ value is higher than that of $k$ by an order of four indicating that the oxidation of $\text{N}_2\text{H}_4$ is 10^4 times swifter than that of $\text{N}_2\text{H}_5^+$ ion. The high reactivity of $\text{N}_2\text{H}_4$ can be ascribed to its molecular structure.

The hydrazine molecule $\text{H}_2\text{N} - \text{NH}_2$ is composed of two tetrahedrons in staggered configuration and one corner of each is occupied by a lone pair of electrons. It can, therefore, act as a dibasic molecule giving rise to both $\text{N}_2\text{H}_4^+$ and $\text{N}_2\text{H}_5^{2+}$ ions. The $\text{N}_2\text{H}_4^+$ ion exists in $\text{N}_2\text{H}_5\text{CO}_4$, which behaves like hydrazinium monooxalate. The $\text{N}_2\text{H}_5^{2+}$ ion is reported to be present in solution of hydrazine sulphate. In the present experimental conditions use of hydrazine perchlorate and acetic acid in buffer strongly indicate the existence of $\text{N}_2\text{H}_5^+$ ion.
The gauche form of hydrazine is considered to be the equilibrium conformation because both the eclipsed and semi eclipsed conformations involve coplanar repulsions. Thus in N₂H₄, two lone pair of electrons are available for coordination. In N₂H₄⁺ ion one of the electron pair is already occupied by the proton and it is likely that the other free lone pair might be polarised towards the other nitrogen bearing the proton and therefore it is not available as such for coordination. Hence the ease of electron transfer and therefore the rate of the reaction seems to be closely related to the availability of lone pair of electron for the formation of a coordinated complex. This also explains the formation of two types of complexes, one with a higher value and the other with a lower value of molar absorptivity compared to that of [CoIIIW]⁶⁻ ion. That the higher rate of oxidation of the species possessing the lone pair has been found to be true in the oxidations of hydroxylamine.

The composite activation parameters cannot be separated. Nevertheless the observed enthalpy and entropy of the activation indicate that the nature of the complex and the nature of the electron transfer within these two complexes is different.

In the "Keggin" structure of K₃[CoIII₃O₁₁W₁₂O₄₅]·20H₂O the central CoIII ion is deeply buried within a shell of WO₆ octahedra (represented by W in the assumed formula) and is, therefore, completely shielded from contact with external species. Therefore, the central CoIII ion is unavailable for direct bonding with the ligand. Hence the formation of an inner-sphere complex in which the ligand is coordinated to the central CoIII atom is highly improbable. The formation of the coordinated complex may therefore involve the ligand and one of the tungstates present in the outer framework. Thus the electron-transfer has to be necessarily through an outer-sphere pathway.

The electron transfer to 12-tungstocobaltate(III) ion during the oxidation process can occur in two ways. One possibility is that the central CoII⁺ atom remains intact and the tungstate framework is reduced as in the oxidation of oxygen and nitrogen containing organic compounds. In the other possibility the outer framework remains intact and the central CoII⁺ atom is reduced as in the oxidation of alkyl aromatic hydrocarbons. The spectrum of the reaction mixture at the end of the reaction was identical with an authentic solution of [CoII⁺W]⁶⁻ ion and the same is true presently as well as in the oxidation of thiocarbonyl acid and hydroxylamine. This suggested that in these oxidations the central tetrahedral CoII⁺ is reduced to CoIII. Since the direct electron-transfer between CoII⁺ and the ligand is unlikely in view of the difficult formation of the inner-sphere complex, the electron transferred to tungstate framework seems to be simultaneously transferred to the central CoII⁺ atom. Although an inner-sphere electron transfer has been suggested in the oxidation of thiocarbonyl acid, the actual mode of electron transfer is not properly understood.

The above argument in favour of an outer-sphere mechanism is sought to be supported by the application of the Marcus cross relation given by Eqs. (14) and (15) where symbols used have their usual meaning.

\[ k_{12} = \left( k_{11} k_{22} f_1 f_2 \right) \]  \hspace{1cm} ... (14)
The oxidation by PtCl₂⁺ might be inner-sphere for the rate was inhibited by chloride ions.  

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References