Kinetics of the Oxidation of Chloride Ions by Tris(2,2′-bipyridine)nickel(III) Ions in Aqueous Perchlorate Media

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The kinetics of oxidation of chloride ions by the tris(2,2′-bipyridine)nickel(III) ion, $[Ni(bipy)_3]^{3+}$, have been investigated in aqueous media. Using conventional spectrophotometry, the orders in the reactant concentrations were found to be variable at an ionic strength of 5.00 mol dm^{-3}. However, using stopped-flow spectrophotometry to investigate the oxidation at an ionic strength of 2.50 mol dm^{-3} at high $[Cl^-]$, the order in $[Ni^{III}]$ was always unity and plots of the pseudo-first-order rate constants × $[Cl^-]^{-1}$ with $[Cl^-]$ at constant acidity were linear with an intercept on the ordinate, and invariant with changes in the acidity. This is interpreted in terms of the involvement of outer-sphere complexes of Cl^- and $[Ni(bipy)_3]^{3+}$ in the mechanism in two parallel pathways. The enthalpies and entropies of activation are compared with those for the oxidation of other substrates by $[Ni(bipy)_3]^{3+}$.

Following our electrolytic preparation of $[Ni(bipy)_3]^{3+}$ (bipy = 2,2′-bipyridine) in aqueous perchlorate media,[1] we have investigated the kinetics of its oxidation of hydrogen peroxide,[1] bromide ions,[2] hydrazoic acid,[3] benzyl alcohol,[4] and DL-1-phenylethanol[5] ions in the same media. The kinetics of the oxidation by $[Ni(bipy)_3]^{3+}$ of $[Fe(H_2O)_6]^{2+}$ and of (3,14-dimethyl-4,7,10,13-tetra-azahexadeca-3,13-diene-2,15-dione)nickel(II) in aqueous trifluoromethanesulphonic acid,[6] of $[Ni(phen)_3]^{2+}$ (phen = 1,10-phenanthroline) in aqueous sulphuric acid,[6] and of VO^{2+}(aq) in aqueous perchlorate media[7] have also been investigated. E.s.r. measurements in frozen mixtures of water with perchloric acid[3] and in frozen acetonitrile solutions[8] at 77 K show that the oxidizing species $[Ni(bipy)_3]^{3+}$ is a genuine complex of Ni^{3+} and not a nickel(II)–radical complex involving a complexed radical of 2,2′-bipyridine. Following our preliminary observation that this oxidizing species of Ni^{3+} with $E^\circ \approx 1.70$ V[6,8] oxidizes chloride ions, we now report our kinetic investigation of this reaction.

Experimental

The $[Ni(bipy)_3]^{3+}$ ion was prepared in solution by electrolytic oxidation, as before.[1] All other materials were described earlier.[1–5] AnalaR HCl or NaCl was used as the source of chloride ions. Slow rates were followed by monitoring changes of absorbance in the thermostatted cell compartment of a Unicam SP 500 Series 2 spectrophotometer, and fast rates using a Durrum-Gibson stopped-flow spectrophotometer with the changes in the absorbance photographed on the storage screen of an oscilloscope. Ionic strength was controlled by the addition of sodium perchlorate, prepared in solution as before.[1–5]

Results and Discussion

Preliminary Observations.—Using an excess of the nickel(III) complex over the chloride ion to determine the stoicheiometry was unsuccessful, owing to the slowness of the reaction under these conditions. It was assumed, therefore, by analogy with the oxidation of bromide ions by this complex, that the consumption ratio $|\Delta[Ni^{III}]|/|\Delta[Cl^-]| = 1.0$.[2]

The first kinetic runs were done at 25.3 °C using the conventional spectrophotometer with a wavelength of 360 nm and at an ionic strength of 5.00 mol dm^{-3}. For $[HClO_4] = 4.00$ mol dm^{-3} with $[Cl^-]$ varying from 0.160 to 0.400 mol dm^{-3} for an initial concentration of the nickel(III) complex of 5×10^{-5} mol dm^{-3}, plots of (absorbance)$^{-1}$ *versus* time gave straight lines (Figure 1), indicating an order of 2 in $[Ni^{III}]$. Second-order rate constants calculated from the slopes varied linearly with $[Cl^-]^2$ (Figure 2) with the plot passing through the origin. Unfortunately, for $[HClO_4]$ = 3.00, 2.00, and 1.00 mol dm^{-3} under similar conditions, neither plots of (absorbance)$^{-1}$ *versus* time nor of log(absorbance) *versus* time gave straight lines, suggesting that the order in $[Ni^{III}]$ was variable. When the ionic strength was reduced to 2.50 mol dm^{-3} for $[HClO_4]$ = 1.00 and 2.00 mol dm^{-3} at 25.3 °C, plots of log(absorbance) against time were linear (Figure 3), showing that the order in $[Ni^{III}]$ under these conditions becomes unity. In order to achieve a wide range of $[Cl^-]$, it was decided to investigate the kinetics at an ionic strength of 2.50 mol dm^{-3} using the stopped-flow technique.

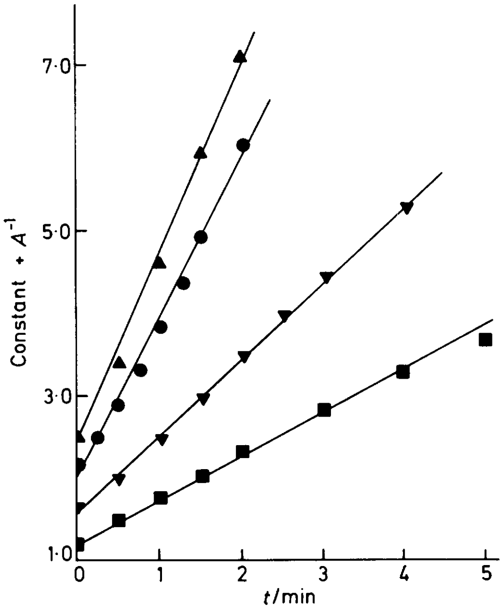

Figure 1. Variation of the reciprocal of the absorbance A with time at 360 nm and 25.3 °C with $[HClO_4]$ = 4.00 mol dm^{-3} at I = 5.00 mol dm^{-3} for the oxidation by $[Ni(bipy)_3]^{3+}$ of various $[Cl^-]$ as follows: (▲) 0.400, constant = 1.00; (●) 0.360, constant = 1.00; (▼) 0.270, constant = 0.50; (■) 0.200 mol dm^{-3}, constant = zero

Rates determined using Stopped-flow Spectrophotometry.—These experiments were all carried out using an ionic strength of

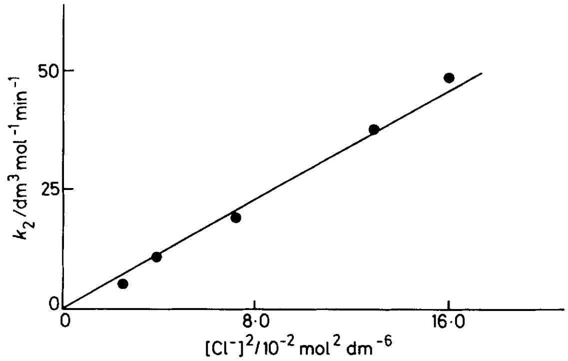

Figure 2. Variation of the observed second-order rate constant k_2 for the oxidation of Cl^- ions by $[Ni(bipy)_3]^{3+}$ with $[Cl^-]^2$ at $[HClO_4]$ = 4.00 mol dm^{-3} and I = 5.00 mol dm^{-3}

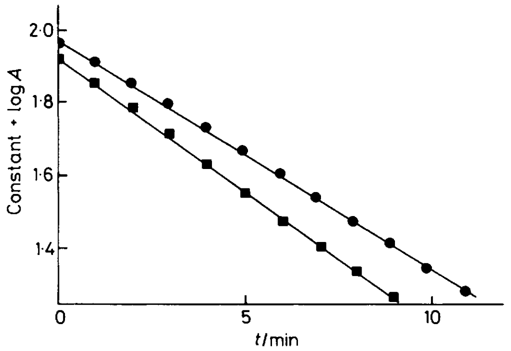

Figure 3. Variation of log(absorbance) against time at 25.3 °C and 360 nm for the oxidation of $[Cl^-]$ = 0.080 mol dm^{-3} by $[Ni(bipy)_3]^{3+}$ at I = 2.50 mol dm^{-3} with varying acidity (/mol dm^{-3}) as follows: (●) 1.00, constant = 2.05; (■) 2.00, constant = 2.00

2.50 mol dm^{-3} and changes in absorbance at 350 nm were followed.

Using an excess of Cl^-, plots of log(absorbance) against time for a constant acidity at 29.6 °C were linear and values for the pseudo-first-order rate constant taken from the slopes are contained in Table 1. Linear plots for the pseudo-first-order rate constant k_0 against $[Cl^-]$ or $[Cl^-]^2$ passing through the origin were not obtained. However, linear plots were obtained for $k_0[Cl^-]^{-1}$ against $[Cl^-]$ with intercepts on the ordinate. These plots for a range of acidities are shown in Figure 4 and it is evident that the slopes and the intercepts are invariant for $[H^+]$ = 0.50—2.50 mol dm^{-3}. This is confirmed by the numerical values obtained for the slopes and intercepts, given in Table 2.

Similar linear plots of $k_0[Cl^-]^{-1}$ against $[Cl^-]$ were obtained at $[H^+]$ = 1.00 and 2.50 mol dm^{-3} for 24.3, 35.3, and 40.6 °C with the ionic strength maintained at 2.50 mol dm^{-3} and the values for k_0 are collected in Table 1. Table 2 shows that both the slopes and the intercepts of these plots are invariant with acidity at constant temperature.

Mechanism of the Oxidation.—The order in $[Cl^-]$ higher than one derived from the plots in Figure 4 suggests that intermediate complexes between the nickel(III) bipyridine complex and the chloride ion must be involved. As the slopes and intercepts are invariant with acidity and there is no evidence that a bipyridine is removed from Ni^{3+},[1-5] it would appear more likely that these are outer-sphere complexes: this is supported by the change in order as the ionic strength increases. Intermediate outer-sphere complexes are postulated as being involved in the oxidation of iodide ions by iron(III) aqua-cations.[9] The form of the plots in Figure 4 suggests that two redox steps are involved, with one containing one more Cl^- in the transition state than the other. If we restrict our discussion to the simplest case, then pre-equilibrium (1) may be involved, followed by redox steps

Table 1. Pseudo-first-order rate constants k_0/s^{-1} for the oxidation of Cl^- ions by $[Ni(bipy)_3]^{3+}$ ions at ionic strength = 2.50 mol dm^{-3}

Temp./ °C	[H$^+$]/ mol dm^{-3}	[Cl$^-$]/mol dm^{-3}					
		0.200	0.400	0.800	1.20	1.50	2.00
24.3	1.00			0.122	0.218	0.322	0.53
24.3	2.50			0.124	0.230	0.340	0.53
29.7	0.50		0.084	0.210	0.384	0.53	0.84
29.7	1.00		0.089	0.207	0.368	0.52	0.86
29.7	1.50		0.087	0.223	0.396	0.53	0.90
29.7	2.50		0.087	0.218	0.368	0.54	0.84
35.3	1.00		0.108	0.266	0.451	0.64	
35.3	2.50		0.110	0.276	0.471	0.66	
40.6	1.00	0.092	0.192	0.451	0.75	0.99	
40.6	2.50	0.087	0.196	0.451	0.75	1.03	

Table 2. Slopes/dm^6 mol^{-2} s^{-1} and intercepts/dm^3 mol^{-1} s^{-1} for the plots of $k_0[Cl^-]^{-1}$ *versus* $[Cl^-]$ at constant acidity with an ionic strength = 2.50 mol dm^{-3}

Temp./°C	[H$^+$]/mol dm^{-3}	Slope	Intercept
24.3	1.00	0.089	0.082
24.3	2.50	0.091	0.086
29.7	0.50	0.130	0.160
29.7	1.00	0.132	0.162
29.7	1.50	0.138	0.160
29.7	2.50	0.130	0.162
35.3	1.00	0.145	0.210
35.3	2.50	0.145	0.220
40.6	1.00	0.157	0.424
40.6	2.50	0.175	0.417

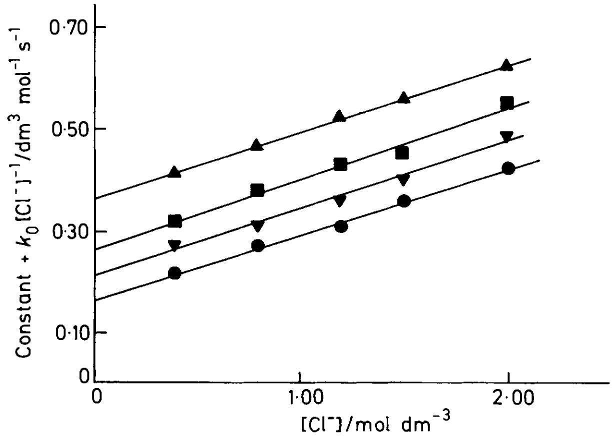

Figure 4. Variation of $k_0[Cl^-]^{-1}$ against $[Cl^-]$ for the oxidation of chloride ions by $[Ni(bipy)_3]^{3+}$ at I = 2.50 mol dm^{-3} and at 29.6 °C with $[HClO_4]$/mol dm^{-3} as follows: (▲) 0.50, constant = 0.200; (▼) 1.00, constant = 0.050; (■) 1.50, constant = 0.100; (●) 2.50, constant = zero

$$Ni^{III} + Cl^- \underset{}{\overset{\beta_1}{\rightleftharpoons}} Ni^{III}Cl^- \qquad (1)$$

(2) and (3) which, in turn, will be followed by the very rapid

$$\mathrm{Ni^{III}Cl^-} \xrightarrow{k_1} \mathrm{Ni^{II}} + \mathrm{Cl^{\bullet}} \qquad (2)$$

$$\mathrm{Ni^{III}Cl^-} + \mathrm{Cl^-} \xrightarrow{k_2} \mathrm{Ni^{II}} + \mathrm{Cl_2}^{\bullet -} \qquad (3)$$

reactions (4) and (5) resulting in the formation of molecular

$$\mathrm{Cl^{\bullet}} + \mathrm{Cl^{\bullet}} \xrightarrow{\text{rapid}} \mathrm{Cl_2} \qquad (4)$$

$$\mathrm{Ni^{III}} + \mathrm{Cl_2}^{\bullet -} \xrightarrow{\text{rapid}} \mathrm{Ni^{II}} + \mathrm{Cl_2} \qquad (5)$$

chlorine. This is analogous to similar proposals concerning the intermediate involvement of similar radical ions in the oxidation of I^- by several aqua-cations,[9–11] the oxidation of Br^- by several aqua-cations,[10–13] and in the oxidation of Cl^- by Co^{III}(aq):[14] there is independent evidence for the existence of the $I_2^{\bullet -}$ radical ion.[15]

The overall decay in the concentration of the nickel(III) bipyridine complex will be given by equation (6) where subscript T indicates the total concentration of Ni^{III}. The pseudo-first-order rate constant will be given by (7). If $\beta_1[Cl^-] \ll 1$,

$$-\frac{d[\mathrm{Ni^{III}}]}{dt} = \frac{k_1\beta_1[\mathrm{Ni^{III}}]_T[\mathrm{Cl^-}]}{1 + \beta_1[\mathrm{Cl^-}]} + \frac{2k_2\beta_1[\mathrm{Ni^{III}}]_T[\mathrm{Cl^-}]^2}{1 + \beta_1[\mathrm{Cl^-}]} = k_0[\mathrm{Ni^{III}}]_T \qquad (6)$$

$$k_0 = \frac{k_1\beta_1[\mathrm{Cl^-}] + 2k_2\beta_1[\mathrm{Cl^-}]^2}{1 + \beta_1[\mathrm{Cl^-}]} \qquad (7)$$

which is plausible for outer-sphere complex formation, a plot of $k_0[Cl^-]^{-1}$ against $[Cl^-]$ will be linear with the slopes and intercepts independent of changes in $[H^+]$. In this case, the intercept = $k_1\beta_1$ and the slope = $2k_2\beta_1$. Plots of $k_1\beta_1$ and $k_2\beta_1$ against the reciprocal of the absolute temperature are linear. Application of the least-squares procedure using a computer produces, for $k_1\beta_1$, $\Delta H^\ddagger = 70 \pm 8$ kJ mol^{-1} and $\Delta S^\ddagger = -29 \pm 27$ J K^{-1} mol^{-1} and, for $k_2\beta_1$, $\Delta H^\ddagger = 25.0 \pm 6.4$ kJ mol^{-1} and $\Delta S^\ddagger = -186 \pm 21$ J K^{-1} mol^{-1}. Although the overall pathway (1) + (3) is favoured energetically over the overall pathway (1) + (2) in reaching the transition state, the latter is disfavoured over the former in respect of the entropy change initial state ⟶ transition state, as expected for an emergent radical ion in (3) as opposed to a radical in (2).

The replacement of reaction (3) by the alternative (8), with

$$\mathrm{Ni^{III}(Cl^-)_2} \xrightarrow{k_2'} \mathrm{Ni^{II}} + \mathrm{Cl_2}^{\bullet -} \qquad (8)$$

both chloride ions already present in the outer sphere of $[Ni(bipy)_3]^{3+}$ prior to the electron transfer, will also fit the kinetic observations. Indeed, the general case involving y chloride ions in the outer sphere of $[Ni(bipy)_3]^{3+}$ with rate-determining electron transfers (9) and (10) where $x \leqslant y$ will

$$\mathrm{Ni^{III}(Cl^-)}_{x-1} \xrightarrow{k_{x-1}} \mathrm{Ni^{II}} + \mathrm{Cl_2}^{\bullet -} + (x-3)\mathrm{Cl^-} \qquad (9)$$

$$\mathrm{Ni^{III}(Cl^-)}_{x} \xrightarrow{k_{x}} \mathrm{Ni^{II}} + \mathrm{Cl_2}^{\bullet -} + (x-2)\mathrm{Cl^-} \qquad (10)$$

also fit the kinetic observations. If β_n is the overall equilibrium constant for (11), k_0 will now be given by (12), which

$$\mathrm{Ni^{III}} + n\mathrm{Cl} \rightleftharpoons \mathrm{Ni^{III}(Cl^-)}_n \qquad (11)$$

will conform with the experimental kinetic observations if

$$k_0 = \frac{2[\mathrm{Cl^-}]^{x-1}(k_{x-1}\beta_{x-1} + k_x\beta_x[\mathrm{Cl^-}])}{1 + \sum_{n=1}^{n=y}\beta_n[\mathrm{Cl^-}]^n} \qquad (12)$$

$(1 + \sum_{n=1}^{n=x-2}\beta_n[Cl^-]^n + \sum_{n=x}^{n=y}\beta_n[Cl^-]^n) \ll \beta_{x-1}[Cl^-]^{x-1}$. As the preliminary rate investigations show, the reaction becomes increasingly complex as the ionic strength increases, including not only the clustering of $[Ni(bipy)_3]^{3+}$ ions with chloride ions but also probably the clustering together of $[Ni(bipy)_3]^{3+}\cdot Cl^-$ complexes.

Table 3. Comparisons of the enthalpies and entropies of activation for the oxidation of substrate ligands by $[Ni(bipy)_3]^{3+}$

Substrate ligand	Comments	$\Delta H^\ddagger$/kJ mol^{-1}	$\Delta S^\ddagger$/J K^{-1} mol^{-1}
H_2O_2	Rate independent of $[H^+]$; no intermediate complex	38 ± 2	-126 ± 7
Br^-	Rate independent of $[H^+]$; no intermediate complex	60 ± 4	-3 ± 11
HN_3 (N_3^-)	Rate $\propto [H^+]^{-1}$; possibly intermediate outer-sphere complex	36 ± 3	-3 ± 10
$C_6H_5CH_2OH$	Rate independent of $[H^+]$; no intermediate complex	77 ± 1	2.0 ± 1.3
$CH_3CH(C_6H_5)OH$	Rate independent of $[H^+]$; no intermediate complex	77 ± 2	-2.4 ± 5.7
Cl^-	$k_1\beta_1$: rate independent of $[H^+]$; intermediate outer-sphere complex	70 ± 8	-29 ± 27
Cl^-	$k_2\beta_1$: rate independent of $[H^+]$; intermediate outer-sphere complex	25 ± 6	-186 ± 21

Comparison with the Oxidation of Chloride Ions by Other Cations.—Chloride ions are oxidized by cobalt(III) aqua-ions[14] and the mechanism involves the intermediate formation of Co^{III}–Cl^- complexes with substitution of the Cl^- ion into the inner sphere of Co^{III}(aq).[16] Inner-sphere complexes of Cl^- with oxidizing cations have also been observed for Fe^{III}(aq),[17] $[Co(NH_3)_2]^{3+}$(aq),[18] $[Co(en)]^{3+}$(aq) (en = ethylenediamine),[19] and $[Ni(macrocycle)]^{3+}$(aq).[20] The independence of rate constants with acidity shows that all the bipyridines remain complexed with the Ni^{3+} in the transition state for the oxidation of Cl^- ions,[1–5] and as the kinetics indicate the involvement of an intermediate $Ni^{III} + Cl^-$ complex it is most likely that it is an outer-sphere complex with the Cl^- remaining outside the co-ordination sphere of the bipyridine ligands. In the oxidation of HN_3 by $[Ni(bipy)_3]^{3+}$ it was suggested[3] that outer-sphere $[Ni(bipy)_3]^{3+}\cdot N_3^-$ complexes may be formed by the dissociation of a proton from the outer-sphere complex $[Ni(bipy)_3]^{3+}\cdot HN_3$.

Values for the overall enthalpies and entropies of activation are compared in Table 3 for all the substrate ligands investigated kinetically in their reactions with $[Ni(bipy)_3]^{3+}$. Comparing the entropies of activation, one notices that those for Br^-, N_3^-, $C_6H_5CH_2OH$, $CH_3CH(C_6H_5)OH$, and Cl^- in processes (1) and (2) are within the limits of their standard errors approximately the same, with perhaps some minor differences among them. The argument that $\Delta S^\ddagger$ values for Br^-, N_3^-, $C_6H_5CH_2OH$, and $CH_3CH(C_6H_5)OH$ are nearly equal and that for H_2O_2 is much more negative has been used to suggest[4,5] that the redox processes for the first four are essentially the same with the transfer of an electron only in the transition state, with the much more negative $\Delta S^\ddagger$ for H_2O_2

arising from the restrictive effects of the emergent H^+ in the transition state for the last case. Comparing the whole set now available in Table 3, the oxidation of Cl^- by processes (1) + (3) and that for H_2O_2 appear to differ from the remainder, including the oxidation of Cl^- by (1) + (2). We conclude, therefore, that, as before, the rate-determining steps for the oxidations of Br^-, N_3^-, $C_6H_5CH_2OH$, and $CH_3CH(C_6H_5)OH$ are all electron transfers, probably from the π orbitals of the benzene rings in the latter two cases, and that the rate-determining step for the oxidation of Cl^- by (1) + (2) is similarly an electron transfer, like that for Br^-, the entropy of activation for all being $\Delta S_e^\ddagger$ for the electron transfer. However, we suggest that the much more negative $\Delta S^\ddagger$ for the oxidation of Cl^- by (1) + (3) arises from a negative contribution, $\Delta S_i^\ddagger$, from the restrictive effects of the emergent radical ion on the solvent molecules: alternatively, or in addition, a negative contribution to $\Delta S^\ddagger$ for reactions (1) + (3) may be incurred from the necessity for orienting three species, Ni^{3+} and two Cl^- ions, in the transition state. As suggested previously,[1–5] the emergent proton will make a negative contribution, $\Delta S_p^\ddagger$, to the overall $\Delta S^\ddagger$, arising from its restrictive effect on the solvent molecules, producing the large overall negative value for $\Delta S^\ddagger$.

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