Kinetics of the Oxidation of Hydrogen Peroxide by the Tris(2,2′-bipyridine)-nickel(III) Ion in Aqueous Perchlorate Media: Comparison with Oxidation by Aqua-cations

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A complex $[Ni(bipy)_3]^{3+}$ has been prepared by the electrolytic oxidation of $[Ni(bipy)_3]^{2+}$. The kinetics of the oxidation of hydrogen peroxide by this complex in aqueous perchlorate media over a temperature range 3.0—40 °C using both conventional and stopped-flow spectrophotometry show that the reaction is first order in $[Ni(bipy)_3{}^{3+}]$, first order in $[H_2O_2]$, and zero order in $[H^+]$. No intermediate complexes are detected, and the zero order in $[H^+]$ shows that the oxidation is not preceded by the substitution of H_2O_2 into the inner sphere of Ni^{3+}. This oxidation is compared with the reaction of H_2O_2 with highly oxidizing aqua-cations.

KINETIC and spectrophotometric evidence shows [1,2] that the equilibria for complex formation between hydrogen peroxide and the aqua-cations $Fe^{III}(aq)$,[3-5] $Ce^{IV}(aq)$,[2,6] $Mn^{III}(aq)$,[2,7] $Co^{III}(aq)$,[2,8] and $Ag^{II}(aq)$ [2,9] are established more rapidly than the rate at which the hydrogen peroxide is decomposed; it is therefore reasonable to suppose [1-10] that these complexes are intermediates in the latter decomposition. The slow step in the oxidation is the first-order decomposition of these intermediates [1-10] and not the rate of formation of the complex.[11] As these cations $M^{n+}(aq)$ exist partially as $M^{n+}OH^-(aq)$ in acidic solutions, and as H_2O_2 has an acid-dissociation constant *ca.* 200 times greater than that for water,[12] an H_2O_2 molecule adjacent to a highly polarizing cation would be expected to exist partially as $[HO_2]^-$; in some cases, these oxidations proceed predominantly by a path involving $M^{n+}HO_2{}^-(aq)$.[1-10] The involvement of $M^{n+}OH^-(aq)$ and $M^{n+}HO_2{}^-(aq)$ is deduced from the form of the variation of the rate with $[H^+]$,[1-10] although it does not distinguish between $M^{n+}OH^-(aq) + H_2O_2$ or dissociation of $M^{n+}H_2O_2(aq)$ for the formation of $M^{n+}HO_2{}^-(aq)$. Kinetic investigations of the oxidation of H_2O_2 by aqua-complexes of Cu^{II} and Co^{III} where the water in the inner-co-ordination sphere is partially replaced by ligands containing nitrogen atoms show that hydrolyzed species $M^{n+}OH^-$ are involved here also, and it is usually assumed that an intermediate complex with H_2O_2 is involved.[13]

In the course of attempts to prepare unusually high oxidation states of transition-metal cations through stabilization by complexing with ligands other than water, $[Ni(bipy)_3]^{3+}$ prepared by the oxidation of tris(2,2′-bipyridine)nickel(II) perchlorate was found to oxidize H_2O_2 at a measurable rate: $Ni^{3+}(aq)$ is too unstable to study any of its reactions in aqueous acidic solutions.[14] This provides an opportunity to investigate the oxidation of hydrogen peroxide by a cation where all the water molecules in the inner-co-ordination sphere have been displaced by non-acidic ligands. If the rate of such a reaction were to be invariant with acidity, it would confirm the interpretation of the acid variations with aqua-cations as being due to the acid dissociation of H_2O and H_2O_2 in the inner sphere of the cations. Whether or not this oxidation proceeds through an intermediate complex is also of interest in view of the apparent necessity [1-10,13] for H_2O_2 to be adjacent to the oxidizing aqua-cation in the transition state.

EXPERIMENTAL

Materials.—A solution of the lime-green tris(2,2′-bipyridine)nickel(III) ion was prepared by anodic oxidation under nitrogen of a suspension of tris(2,2′-bipyridine)-nickel(II) perchlorate in 2.0 mol dm^{-3} $HClO_4$ at 5 °C. Perchloric acid was of AnalaR grade; solutions of sodium and lithium perchlorate were prepared by neutralization of AnalaR $HClO_4$ with AnalaR $Na_2[CO_3]$ and AnalaR $Li_2[CO_3]$ respectively. G. F. Smith magnesium perchlorate was used. Solutions of tris(2,2′-bipyridine)iron(II) sulphate were prepared by dissolving the calculated weights of AnalaR $Fe[SO_4]\cdot 7H_2O$ and 2,2′-bipyridine in distilled water. Water was distilled once in an all-glass still. Solutions of hydrogen peroxide were prepared by the dilution of 80% stabilizer-free H_2O_2 from Laporte and Co.

Analytical Methods.—Concentrations of Ni^{III} were determined by rapidly mixing the solution with a solution of

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excess of $[Fe(bipy)_3]^{2+}$ and estimating the decrease in the concentration of the latter ion spectrophotometrically at 522 nm using $\varepsilon = 8.65 \times 10^3$ dm^3 mol^{-1} cm^{-1}; the $[Fe(bipy)_3]^{3+}$ produced (ε 125 dm^3 mol^{-1} cm^{-1}) does not interfere with this determination.[14] The concentration of hydrogen peroxide in stock solutions was determined by titration with Ce^{IV} using ferroin as indicator.

Kinetic Measurements.—Conventional rates were followed in the thermostatted cell compartment of a Unicam SP 500 series 2 spectrophotometer equipped with an external flat-bed recorder. Fast reaction rates were followed in a Durrum–Gibson stopped-flow spectrophotometer, and the reaction trace was photographed on the storage screen of a Tektronix oscilloscope. The temperature required was attained by circulation of water from a thermostat or of an ethanol–water mixture from a cryostat.

Preliminary rate measurements show that $[Ni(bipy)_3]^{3+}$ was stable in concentrated solutions of $HClO_4$, but that it oxidized water at low $[HClO_4]$.[14] Runs with H_2O_2 present were only carried out where the loss of Ni^{III} through the oxidation of water never exceeded 5% of the total Ni^{III}: in most cases, loss of Ni^{III} from this cause was much less than 5% during the run. A solution of $[Ni(bipy)_3]^{3+}$ has a very weak absorbance maximum at *ca.* 550 nm, with the absorbance increasing continuously from 450 to 325 nm; below 325 nm, $[Ni(bipy)_3]^{2+}$ interferes considerably with the absorbance from $[Ni(bipy)_3]^{3+}$.[14] Rate measurements were usually made at 350 nm where $\varepsilon \sim 7 \times 10^3$ for $[Ni(bipy)_3]^{3+}$ and $\varepsilon \sim 370$ dm^3 mol^{-1} cm^{-1} for $[Ni(bipy)_3]^{2+}$. The cation $[Ni(bipy)_3]^{2+}$ is solvolyzed rapidly in these strongly acidic solutions and in the runs with conventional rates the product is usually $Ni^{2+}(aq)$, but any delay in this latter reaction relative to the oxidation of H_2O_2 causes negligible errors in the optical density measured against a blank of distilled water. In the stopped-flow experiments the product observed is usually $[Ni(bipy)_3]^{2+}$: any error arising from the solvolysis of $[Ni(bipy)_3]^{2+}$ between the initial adjustment of the base line of the oscilloscope for reaction products and the return of the trace to this base line following an oxidation never exceeded 2%.

RESULTS AND DISCUSSION

Stoicheiometry.—It was not possible to determine the consumption of $[Ni(bipy)_3]^{3+}$ by H_2O_2 in conditions where $[Ni^{III}] > [H_2O_2]$ in the $[HClO_4]$ used for the kinetic measurements owing to the high errors arising from the oxidation of water by Ni^{III}. It is therefore assumed that the overall stoicheiometry of this reaction is analogous to that of similar oxidations of H_2O_2[2,6-9,11,13b] where the product cation does not also reduce H_2O_2, as in (1).

$$2Ni^{III} + H_2O_2 \longrightarrow 2Ni^{II} + O_2 + 2H^+ \qquad (1)$$

Preliminary Kinetic Measurements.—The first conventional rates were determined at 21.0 °C at 360 nm in conditions where the $[H_2O_2]$ was in a large excess over the initial $[Ni^{III}]$ with the ionic strength I maintained at 5.00 mol dm^{-3} by the addition of sodium perchlorate. Plots of log(optical density) against time were always linear, and a plot of the pseudo-first-order rate constant k_0 taken from the gradients against $[H_2O_2]$ at 5.00 mol dm^{-3} $HClO_4$ was linear. Therefore the reaction is first order in $[Ni^{III}]$ and first order in $[H_2O_2]$: values for the second-order rate constant k_2 increased from 2.34×10^{-2} dm^3 mol^{-1} s^{-1} in 5.00 mol dm^{-3} $HClO_4$ to 4.06×10^{-2} dm^3 mol^{-1} s^{-1} in 1 mol dm^{-3} $HClO_4$ at $I = 5.00$ mol dm^{-3} maintained with added $Na[ClO_4]$. However, in runs where initial $[Ni^{III}] = 5 \times 10^{-5}$ mol dm^{-3}, initial $[H_2O_2] = 9.8 \times 10^{-2}$ mol dm^{-3} in 3.60 mol dm^{-3} $HClO_4$, and with the same initial concentrations of Ni^{III} and H_2O_2 but with $[HClO_4] = 1.60$ mol dm^{-3} and $I = 3.60$ mol dm^{-3} adjusted by the addition of $Li[ClO_4]$, $Na[ClO_4]$, or $Mg[ClO_4]_2$, the respective values for k_0 at 21.0 °C were (in 10^3 s^{-1}) 1.46, 1.68, 1.82, and 2.88. This suggests that the above apparent small change in rate with changing $[HClO_4]$ at $I = 5.00$ mol dm^{-3} may arise from the specific effect of changing H^+ for Na^+ in the solution. All the subsequent runs were performed at $I = 2.00$ mol dm^{-3} with added $Li[ClO_4]$ to provide a reasonable variation in $[HClO_4]$ with a minimal specific-ion effect: no differences in rate were found at $I = 2.00$ mol dm^{-3} between added $Li[ClO_4]$ or added $Na[ClO_4]$.

Rate Measurements with Added $Li[ClO_4] + HClO_4$ *at Ionic Strength* = 2.00 mol dm^{-3}.—Under all the conditions investigated, a large excess of $[H_2O_2]$ over initial $[Ni^{III}]$ was used. For the stopped-flow runs, the initial $[Ni^{III}] \sim 1 \times 10^{-4}$ mol dm^{-3}, and for the conventional runs the initial $[Ni^{III}] \sim 5 \times 10^{-5}$ mol dm^{-3}. None of the traces from the stopped-flow experiments suggested the participation of a rapid pre-equilibrium between the reactants. In general, the stopped-flow traces were recorded for 350 nm, and the change in optical density in the conventional runs was followed at 360 nm.

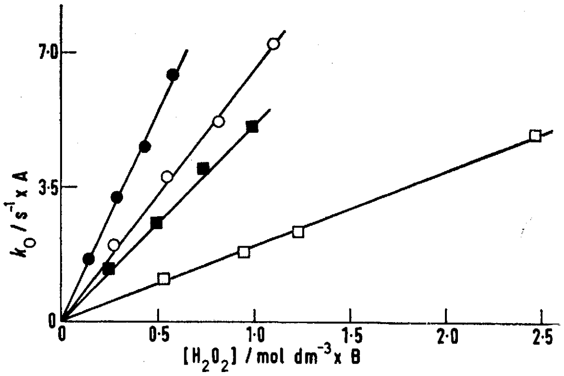

FIGURE 1 Plots of k_0 against $[H_2O_2]$ at $[HClO_4] = 2.00$ and $I = 2.00$ mol dm^{-3} at various temperatures: (●), 32.0 °C, A = 10, B = 1.0; (○), 24.3 °C, A = 10, B = 1.0; (■), 18.0 °C, A = 1.0 × 10^3, B = 1.0 × 10^2; and (□), 3.0 °C, A = 1.0 × 10^3, B = 1.0 × 10^2

At 24.3 °C the rates were accessible to both conventional and stopped-flow spectrophotometry, depending on the conditions. The plots of log(optical density) against time were linear, and Figure 1 shows that k_0 plotted against $[H_2O_2]$ at constant $[HClO_4]$ gives a straight line passing through the origin. Similar linear plots of log(optical density) against time were obtained for a range of temperatures, and Figure 1 shows that plots of k_0 against $[H_2O_2]$ at constant $[HClO_4]$

are linear at constant temperature. At 3.0 and 18.0 °C, conventional spectrophotometry was used to follow the rates, and stopped-flow spectrophotometry was used at 32.0 and 40.2 °C. The value of the second-order rate constant k_2 is invariant with acidity at each temperature. The average values for k_2 at each temperature recorded in the Table give a straight line in Figure 2 for the plot of log k_2 against the reciprocal of the absolute temperature. From the gradient of Figure 2 computed by the least-squares procedure, the energy of activation $E = 40 \pm 2$ kJ mol^{-1}; the entropy of activation $\Delta S^{\ddagger} = -126 \pm 7$ J K^{-1} mol^{-1} at 25.0 °C.

Values of k_2 at $I = 2.00$ mol dm^{-3} with added Li[ClO$_4$]

θ_c/°C	[HClO$_4$]/mol dm^{-3}	10^3[H$_2$O$_2$]/mol dm^{-3}	k_2/dm^3 mol^{-1} s^{-1}
3.0	1.00—2.00	5.3—24.6	0.096 ± 0.003
16.0	0.50—2.00	2.46—12.3	0.26 ± 0.01
24.3	0.50—2.00	4.92—1 100	0.34 ± 0.02
32.0	0.50—2.00	144—580	0.56 ± 0.01
40.2	1.00—2.00	144—288	0.72 ± 0.04

Mechanism of the Oxidation of H_2O_2 *by Cations.*—Although, as with the oxidatively unstable [Ni(NH$_3$)$_6$]$^{3+}$, [Ni(en)$_3$]$^{3+}$ (en = ethylenediamine), and [Ni(glycine)$_3$]$^{3+}$,[15] direct analytical identification of the complex used here is not possible, one can show that there is little doubt that it is [Ni(bipy)$_3$]$^{3+}$. The maximum number of bipy molecules attached to cations in this area of the Periodic Table is three.[16,17] Equilibrium measurements [18,19] in aqueous solution show that β = [M(bipy)$_3$]/[M][bipy]^3 (M = cation) is very high for these complexes: in particular, $\beta = 2.88 \times 10^{18}$ dm^9 mol^{-3} at 25 °C in 1 mol dm^{-3} Na[ClO$_4$] for M = Ni^{II},[18] the precursor of our complex, and $\beta = 1.05 \times 10^{16}$ dm^9 mol^{-3} at 20 °C in 0.1 mol dm^{-3} Na[NO$_3$] for M = Co^{II},[19] the ion isoelectronic with Ni^{III}. Spectral and crystallographic examinations [20] and other measurements [17] show that these complexes exist as distorted octahedra with both nitrogen atoms of all the three bipyridines attached to the metal. Further, our complex, on reduction at 0 °C in aqueous perchlorate media, yields a precipitate of [Ni(bipy)$_3$][ClO$_4$]$_2$. Therefore, as both the precursor to our complex and the product of its reduction are [Ni(bipy)$_3$]$^{2+}$, it is highly unlikely that our complex has anything but three bipyridines attached, involving all the nitrogen atoms: as indicated below, any removal of a nitrogen atom from the metal as a preliminary to oxidation of H$_2$O$_2$ would require the rate of oxidation to vary with acidity, which is contrary to observation.

The low solubility [14] of [Ni(bipy)$_3$]$^{2+}$ in aqueous perchlorate media combined with the oxidative instability of the higher redox state prevent high yields of the latter being obtained in the electrolysis. The high $E^{\ominus}$ estimated for the Ni^{II}(aq)–Ni^{III}(aq) couple (3.1—5.5 V) [21] suggest that it is unlikely that any redox state higher than Ni^{III} can be formed electrolytically. The oxidation by Cl$_2$ and Br$_2$ in solution of octahedral complexes of Ni^{II} with ligands chelated through N atoms produces [22] low-spin d^7 Ni^{III}; but these reagents will not oxidize [Ni(bipy)$_3$]$^{2+}$.[23] Similarly, oxidation by electrolysis, HNO$_3$, or [NO][BF$_4$] of Ni^{II} complexes with square-planar cyclic amines [24] produces low-spin d^7 Ni^{III}, as does the oxidation of Ni^{II} in [NiX$_3$(PR$_3$)$_2$] (X = Cl or Br; R = Me, Et, Pr, or Bu) [25] and in [NiCl$_2$(pdma)$_2$]Cl [pdma = *o*-phenylenebis(dimethylarsine)].[26] Nickel(IV) is only detected as a product in the electrochemical oxidation of fluoronickel(II) complexes [27] or in the further oxidation of Ni^{III} in [NiCl$_2$(pdma)$_2$]Cl$_2$ using concentrated HNO$_3$; [28] but the electrochemical oxidation of Ni^{II} in 85% K[OH] yields only Ni^{III}.[29] We therefore conclude that there can be little doubt that the redox state of our complex is Ni^{III}. This is supported by the absence of any observation of a redox state intermediate between our complex and Ni^{II} in the oxidations involving a range of substrates.[14]

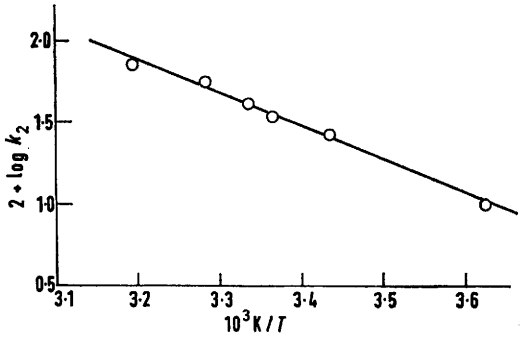

FIGURE 2 Plot of log k_2 against the reciprocal of the absolute temperature

Unlike the oxidation of hydrogen peroxide by highly oxidizing aqua-cations,[1-10] there is no evidence for the formation of a (cation + H$_2$O$_2$) complex in the oxidation by [Ni(bipy)$_3$]$^{3+}$. The zero order in [H$^+$] shows that the bimolecular interaction between solvated [Ni(bipy)$_3$]$^{3+}$

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and H_2O_2 is not controlled by a slow replacement of a ligand on Ni^{III} by H_2O_2. Such a replacement would consist of a slow aquation followed by a rapid anation with H_2O_2, and the aquations of $[Fe(bipy)_3]^{2+}$ (refs. 30 and 31) and $[Ni(bipy)_3]^{2+}$ (refs. 31 and 32) and of related complexes [31] are catalyzed by protons requiring the rate of aquation to increase with increasing $[H^+]$. This is supported by the observation [14] that $[Ni(bipy)_3]^{3+}$ is stable at high acidities, and that its rate of disappearance in the absence of added substrate increases with decreasing acidity.[14] The latter reaction is almost certainly the oxidation of water by $[Ni(bipy)_3]^{3+}$, an oxidation which occurs with aqua-cations having a high redox potential, *e.g.* $Co^{III}(aq)$ (refs. 8 and 33) and $Ag^{II}(aq)$.[34] The absence of an acid dependence for the oxidation of H_2O_2 by $[Ni(bipy)_3]^{3+}$, where there is no H_2O or H_2O_2 adjacent to the polarizing cation to provide $[OH]^-$ and $[HO_2]^-$ in the inner-co-ordination sphere, supports the mechanisms proposed for the oxidation by $Co^{III}(aq)$ and $Fe^{III}(aq)$, as discussed above.

The values of E and $\Delta S^{\ddagger}$ for the oxidation relate to the rearrangement of the system, including the solvation, in the transition state sufficient to enable electron tunnelling to occur between the ligand and cation. The large *overall* positive $\Delta S^{\ddagger}$ for $M^{n+}(aq) + H_2O_2$ with $M^{n+}(aq) = Co^{III}(aq)$ (E 88 kJ mol^{-1}; $\Delta S^{\ddagger}$ 69 J K^{-1} mol^{-1}),[2] $Fe^{III}(aq)$ (E 152 kJ mol^{-1}; $\Delta S^{\ddagger}$ 105 J K^{-1} mol^{-1}),[3,10] and *cis*-$[Co(NH_3)_2]^{3+}(aq)$ [13b] arises from the loss of restriction on the solvent by the cation required to facilitate the charge change accompanying the electron transfer in the transition state, $\Delta S_{elec.}^{\ddagger}$, dominating the increase in restriction imposed on the solvent by the proton released from H_2O_2, $\Delta S_{prot.}^{\ddagger}$, *i.e.* $|\Delta S_{elec.}^{\ddagger}| > |\Delta S_{prot.}^{\ddagger}|$. In contrast, for the large negative overall $\Delta S^{\ddagger}$ of $[Ni(bipy)_3]^{3+} + H_2O_2$, $|\Delta S_{prot.}^{\ddagger}| > |\Delta S_{elec.}^{\ddagger}|$: $\Delta S_{elec.}^{\ddagger}$ is smaller than for $M^{n+}(aq)$ due to the remoteness of the water molecules from the centre of the charge in $[Ni(bipy)_3]^{3+}$. By analogy with $Co^{III}(aq)$ and $Fe^{III}(aq)$,[2,3] it has been assumed [2,6,7] that the preferred path involves $M^{n+}HO_2^-$ rather than $M^{n+}H_2O_2$ for $M^{n+} = Mn^{III}(aq)$, $Ce^{IV}(aq)$, and $Ag^{II}(aq)$, requiring a positive $\Delta S^{\ddagger}$ with $\Delta S_{prot.}^{\ddagger}$ absent for this individual oxidative step. However, the observed large negative $\Delta S^{\ddagger}$ accompanying $E \sim 0$ for this step could arise if (2)

$$M^{n+}H_2O_2(aq) \longrightarrow M^{(n-1)+}(aq) + HO_2^{\cdot} + H^+(aq) \quad (2)$$

operates for these latter cations with $|\Delta S_{prot.}^{\ddagger}| > |\Delta S_{elec.}^{\ddagger}|$ and simultaneous electron and proton transfers rather than the sequential transfers preferred by $Co^{III}(aq)$ and $Fe^{III}(aq)$ involving the ligand $[HO_2]^-$. Alternatively, if $[HO_2]^-$ in the complex for $M^{n+} = Mn^{III}(aq)$, $Ce^{IV}(aq)$, and $Ag^{II}(aq)$ only partly penetrates the aqua-sheath of $M^{n+}(aq)$, sufficiently to modify its molecular orbital system and spectrum, the negative $\Delta S^{\ddagger}$ may arise from internal restrictions produced by a contraction of the $M^{n+} + [HO_2]^-$ distance in the transition state.[35] The relation of $Co^{III}(aq) + H_2O_2$ to the sequence of $E^{\ominus}$ for $M^{n+}(aq)$ has already been discussed.[2]

It is not surprising that, as changes in the arrangement of water molecules near M^{n+} play such a large part in these oxidations, the rates and transition-state parameters for oxidation are similar [11] to (but not equal to) those for substitution by oxidatively inert ligands, which is also largely controlled by the movement of water molecules in the vicinity of a cation.

[6/1784 *Received*, 23*rd September*, 1976]

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