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# Oxidations of hydrogen peroxide by bis(1,4,7-triazacyclononane)-nickel(III), bis(1,4,7-trithiacyclononane)iron(III) and tris(2,2′-bipyridine)ruthenium(III) ions in acidic aqueous solutions ‡

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The oxidations of hydrogen peroxide by typical outer-sphere oxidizing reagents, bis(1,4,7-triazacyclononane)nickel(III) [$Ni(tacn)_2^{3+}$], bis(1,4,7-trithiacyclononane)iron(III) [$Fe(ttcn)_2^{3+}$], and tris(2,2′-bipyridine)ruthenium(III) [$Ru(bipy)_3^{3+}$], were studied in acidic aqueous solution [ionic strength $I = 0.10$ mol $dm^{-3}$ ($NaClO_4$)]. The stoichiometry was determined iodometrically as 2:1 ($[M^{III}]:[H_2O_2]$) for the reactions of $[Ni(tacn)_2]^{3+}$ and $[Fe(ttcn)_2]^{3+}$. Kinetic measurements with an excess of $H_2O_2$ revealed that $HO_2^-$ is the only redox-active species for the reaction with $[Ni(tacn)_2]^{3+}$ under the conditions $2 < -\log[H^+] < 5.5$, while the participation of both $HO_2^-$ and $H_2O_2$ was observed for the reactions with $[Fe(ttcn)_2]^{3+}$ and $[Ru(bipy)_3]^{3+}$. The second-order rate constant for the oxidation reaction of $HO_2^-$ by $Ni(tacn)_2^{3+}$ was $(6.15 \pm 0.06) \times 10^6$ $dm^3$ $mol^{-1}$ $s^{-1}$ at 25 °C with $\Delta H^‡ = 46.9 \pm 0.4$ kJ $mol^{-1}$ and $\Delta S^‡ = 42 \pm 1$ J $K^{-1}$ $mol^{-1}$. The rate constants for the oxidation of $HO_2^-$ and $H_2O_2$ by $[Fe(ttcn)_2]^{3+}$ at 25 °C were $(2.63 \pm 0.18) \times 10^9$ $dm^3$ $mol^{-1}$ $s^{-1}$ with $\Delta H^‡ = 26.7 \pm 4.1$ kJ $mol^{-1}$ and $\Delta S^‡ = 25 \pm 14$ J $K^{-1}$ $mol^{-1}$, and $3.12 \pm 0.03$ $dm^3$ $mol^{-1}$ $s^{-1}$ with $\Delta H^‡ = 40.1 \pm 0.9$ kJ $mol^{-1}$ and $\Delta S^‡ = -101 \pm 3$ J $K^{-1}$ $mol^{-1}$, respectively. The rate constants for the oxidation reaction of $HO_2^-$ and $H_2O_2$ by $[Ru(bipy)_3]^{3+}$ at 25 °C were $(3.70 \pm 0.26) \times 10^7$ and $3.57 \pm 0.19$ $dm^3$ $mol^{-1}$ $s^{-1}$, respectively. It was confirmed from the Marcus-type cross-relation that the oxidations of $HO_2^-$ by $[Fe(ttcn)_2]^{3+}$ and $[Ru(bipy)_3]^{3+}$ proceed through the outer-sphere mechanism with $k_{ex}(HO_2^{\bullet}–HO_2^-) = 3.8 \times 10^{-3}$ $dm^3$ $mol^{-1}$ $s^{-1}$. The second-order rate constant for the oxidation of $HO_2^-$ by $[Ni(tacn)_2]^{3+}$ was *ca.* $10^3$ times faster than the predicted rate constant from the other outer-sphere reactions. The kinetic isotope effect ($k_H/k_D = 2.8$) indicates that the reaction of $HO_2^-$ with $[Ni(tacn)_2]^{3+}$ proceeds *via* a transition state (shown in Scheme 1). The difference in the reactivity of small ions is discussed in relation to the electronic coupling in the precursor complex and the solvation structures of small ions.

Reactions of hydrogen peroxide in aqueous acidic solutions have been intensively studied for the elucidation of the reaction mechanism of this analytically and biochemically important reagent.[1–4] Most of these studies concern the inner-sphere reactions of hydrogen peroxide with metal aqua complexes, in which the electron-transfer processes were significantly accelerated by the formation of metal–peroxide bonds.

Wells and Fox[5] investigated the one-electron oxidation reaction of hydrogen peroxide with the substitution-inert tris(2,2′-bipyridine)nickel(III) ion $[Ni(bipy)_3]^{3+}$ in aqueous acidic solutions, which was independent of $[H^+]$ (> 0.5 mol $dm^{-3}$) and no replacement of the ligand on the nickel(III) center by $H_2O_2$ was observed. As the $pK_a$ value of hydrogen peroxide is 11.52 at 298 K, the species which reacted with $[Ni(bipy)_3]^{3+}$ was supposed to be $H_2O_2$ rather than the more reactive $HO_2^-$ below pH 0.3.[6] Macartney and Sutin[7] investigated the electron-exchange reaction for the $[Ni(bipy)_3]^{3+/2+}$ couple in acidic aqueous solutions, and reported that the redox potential and the electron-exchange rate constant for this couple were 1.72 V ($[CF_3SO_3H] = 1$ mol $dm^{-3}$) and $1.5 \times 10^3$ $dm^3$ $mol^{-1}$ $s^{-1}$, respectively. Using the redox potential of 1.44 V for the $H_2O_2$–$HO_2^{\bullet}$ couple,[6] a value of $2.5 \times 10^{-9}$ $dm^3$ $mol^{-1}$ $s^{-1}$ can be estimated for the electron-exchange reaction between $H_2O_2^{\bullet+}$ and $H_2O_2$ at $[H^+] = 1$ mol $dm^{-3}$, by assuming the $pK_a$ value of equilibrium (1) to be 1.0.[8a]

$$H_2O_2^{\bullet+} \rightleftharpoons H^+ + HO_2^{\bullet};\ pK_a = -1\ ^{8b}\text{ or } 1.0 \qquad (1)$$

More recently, Macartney[9] reported that the oxidation reactions of $H_2O_2$ by tris(polypyridine)metal(III) complexes (M = Fe, Ni or Os) occur *via* an outer-sphere mechanism under neutral or basic conditions, by carrying out careful experiments at $6 < pH < 9$. Although a possible decomposition of polypyridine ligands by $OH^-$ has been suggested,[10] his precise experiments revealed that the reduction of the metal(III) center by $HO_2^-$ takes place more rapidly compared with ligand decomposition in the basic media. Macartney estimated the electron self-exchange rate constant for the $HO_2^{\bullet}$–$HO_2^-$ couple as *ca.* 0.01 $dm^3$ $mol^{-1}$ $s^{-1}$.

We have studied the reactions of hydrogen peroxide with $[Ni(tacn)_2]^{3+}$ and $[Fe(ttcn)_2]^{3+}$ (tacn = 1,4,7-triazacyclononane, ttcn = 1,4,7-trithiacyclononane) to examine the possible reaction pathways for the oxidation of hydrogen peroxide in acidic solutions. The reaction of $HO_2^-$ with the latter complex is expected to proceed through an outer-sphere mechanism while that with the $[Ni(tacn)_2]^{3+}$ complex may take place through a pathway involving the interaction between $HO_2^-$ and the amino hydrogen atom on the tacn ligand. By the use of two structurally similar complexes, $[Ni(tacn)_2]^{3+}$ and $[Fe(ttcn)_2]^{3+}$, the involvement of the hydrogen atom in the electron-transfer process may be examined. The stoichiometries of the reactions were determined iodometrically. The oxidation of hydrogen peroxide by $[Ru(bipy)_3]^{3+}$ was also studied for direct comparison of the kinetic data with those reported by Macartney.[9] The kinetic isotope effect was also examined to confirm the interaction of $HO_2^-$ with the amino hydrogen atom on the tacn ligand during the electron-transfer process. This provides an opportunity to investigate the reactivity of $H_2O_2$ and $HO_2^-$ ions in detail.

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‡ *Supplementary data available* (No. SUP 57287, 6 pp.): rate constants for the oxidations. See *J. Chem. Soc.*, *Dalton Trans.*, 1997, Issue 1.

## Experimental

### Syntheses

The complex $[Ni(tacn)_2][ClO_4]_3$ was synthesized according to the literature method[11] (Found: C, 23.77; N, 13.75; N, 4.88. Calc. for $C_{12}H_{30}Cl_3N_6NiO_{12}$: C, 23.42; N, 13.66; H, 4.91%). The complexes $[Fe(ttcn)_2][ClO_4]_2$ and $[Fe(ttcn)_2][ClO_4]_3$ were synthesized by the literature methods[12,13] (Found: C, 23.99; N, 0.03; H, 3.99. Calc. for $C_{12}H_{24}Cl_2FeO_8S_6$: C, 23.42; N, 0; H, 3.93. Found: C, 21.02; N, 0; H, 3.53. Calc. for $C_{12}H_{24}Cl_3FeO_{12}S_6$: C, 20.16; N, 0; H, 3.38%) and $[Ru(bipy)_3][ClO_4]_3$ was synthesized by oxidizing $[Ru(bipy)_3]Cl_2$ with $Cl_2$.[10] By the addition of sodium perchlorate solution, dark green crystals were obtained, which were washed with ethanol and diethyl ether, and dried *in vacuo* (Found: C, 39.04; N, 8.97; H, 3.25. Calc. for $C_{30}H_{24}Cl_3N_6O_{12}Ru$: C, 41.51; N, 9.68; H, 2.79%). The poor microanalysis results for the $[Fe(ttcn)_2][ClO_4]_3$ and $[Ru(bipy)_3][ClO_4]_3$ were caused by the existence of unchanged $[Fe(ttcn)_2][ClO_4]_2$ or $[Ru(bipy)_3][ClO_4]_2$.[14] However, under the pseudo-first-order conditions used in this study, the existence of iron(II) or ruthenium(II) species (up to 23% was determined spectrophotometrically[14]) did not interfere in the oxidation reactions of hydrogen peroxide.

### Chemicals

Stabilizer-free hydrogen peroxide (Mitsubishi Gas Co.) was used without further purification. Analyses by standardized permanganate solution revealed that the solution supplied contained 31.10% $H_2O_2$. Sodium perchlorate was prepared by mixing perchloric acid (SSG grade, Wako Pure Chemicals) and sodium carbonate (AR grade, Wako). After two recrystallizations, a stock solution was prepared by dissolving the solid in doubly distilled water. Its concentration was determined gravimetrically. Deuterium oxide (99.8 atom %) and deuteriated perchloric acid (68%, $D_2O$) were obtained from Aldrich. Other chemicals (AR grade, Wako) were used without further purification.

### Physical measurements

Kinetic measurements of the oxidation of hydrogen peroxide by $[Ni(tacn)_2]^{3+}$ were carried out with excess amounts of hydrogen peroxide by using a Unisoku RA-401 stopped-flow apparatus ($4 < -\log[H^+] < 6$) and by using a JASCO Ubest V-570 UV/VIS spectrophotometer ($2 < -\log[H^+] < 3$). The temperatures of the cell compartments of each apparatus were controlled to ± 0.1 °C by a Hetofrig 04-PT-623 and by a Neslab RTE-111 temperature controller, respectively. Hydrogen-ion concentrations of sample solutions were adjusted either by the addition of perchloric acid or by acetic acid–sodium acetate buffer solutions (0.04 mol $dm^{-3}$). The decrease in the absorption of $[Ni(tacn)_2]^{3+}$ was monitored at 312 nm. The oxidation of hydrogen peroxide by $[Fe(ttcn)_2]^{3+}$ was monitored at 340 nm in acidic solutions ($[H^+] = 8.12 \times 10^{-3}$–$3.05 \times 10^{-2}$ mol $dm^{-3}$). The reaction of hydrogen peroxide with $[Ru(bipy)_3]^{3+}$ was studied in the range $3.91 < -\log[H^+] < 6.63$ by using acetic acid–sodium acetate (0.04 mol $dm^{-3}$) and phosphoric acid–sodium phosphate buffer solutions (0.04 mol $dm^{-3}$) by monitoring the absorbance change at 452 nm.

A kinetic isotope effect was observed for the oxidation of hydrogen peroxide by $[Ni(tacn)_2]^{3+}$ in $D_2O$ at $[D^+] = 1.00 \times 10^{-2}$ mol $dm^{-3}$ ($DClO_4$). The $pK_D$ value for reaction (3) was

$$H_2O_2 \overset{K_H}{\rightleftharpoons} H^+ + HO_2^- \quad (2)$$

$$D_2O_2 \overset{K_D}{\rightleftharpoons} D^+ + DO_2^- \quad (3)$$

estimated from the linear relationship between $K_H$ and $K_D$ for various acids and bases reported to date.[15]

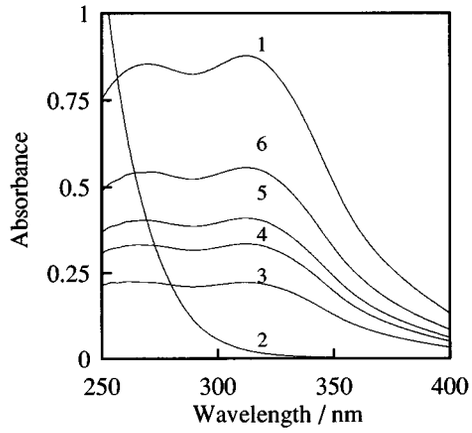



**Fig. 1** Recovery of $[Ni(tacn)_2]^{3+}$ by re-oxidation of a solution containing $[Ni(tacn)_2]^{2+}$ with peroxodisulfate. 1; Original absorption spectrum before the reaction with $H_2O_2$. 2; Spectrum after completion of reduction of 1 by $H_2O_2$ (30 min after the reduction under neutral conditions). 3–6; Reappearance of $[Ni(tacn)_3]^{3+}$ at 20, 40, 60 and 260 min after the addition of excess of peroxodisulfate to 2 at pH 1 (perchloric acid), respectively. Spectra 3–6 were calculated by subtracting 2 from the absorption spectra recorded at each time interval. $[Ni(tacn)_2^{3+}]_0 = 9.03 \times 10^{-5}$ mol $dm^{-3}$, $[H_2O_2]$ added $= 5.96 \times 10^{-2}$ mol $dm^{-3}$

As the 31.10% solution of $H_2O_2$ in $H_2O$ was used to prepare the $D_2O_2$ solution, the formation of deuteriated hydrogen peroxide was not complete (maximum molar ratio of $H_2O:D_2O$ 1:30). However, after 1 h, the deuterium oxide solution containing $H_2O_2$ gave reproducible kinetic data for the reaction with $[Ni(tacn)_2]^{3+}$, which suggests that the substitution of hydrogen ion for deuterium ion was in complete equilibrium within an hour. It has been reported by McAuley *et al.*[11] that the amino protons on co-ordinated tacn rapidly exchange with deuterium ions in solution. Therefore, the kinetic isotope effect can be successfully observed if there is any significant interaction between hydrogen peroxide and the hydrogen atom on the amino nitrogen of the tacn ligand.

### Determination of the stoichiometries

The stoichiometry of the oxidation of hydrogen peroxide by $[Ni(tacn)_2]^{3+}$ was determined by the following method. To a hydrogen peroxide solution, the concentration of which was determined iodometrically, was added a weighed amount of solid $[Ni(tacn)_2][ClO_4]_3$. After the reaction was complete (up to 1 h which corresponds to more than 100 half-lives), the amount of excess of hydrogen peroxide was determined iodometrically. This procedure was repeated three times and the stoichiometry determined as $2.01 \pm 0.01:1$ for $[Ni(tacn)_2^{3+}]:[H_2O_2]$. Therefore, the overall reaction is expressed by equation (4).[5]

$$2[Ni(tacn)_2]^{3+} + H_2O_2 \longrightarrow 2[Ni(tacn)_2]^{2+} + O_2 + 2H^+ \quad (4)$$

The reversibility of the reaction was examined by the spectrophotometric method. After completion of the reaction, the reaction mixture was treated with an excess amount of peroxodisulfate. The increase of the absorption bands at 270 and 310 nm in Fig. 1 indicates the recovery of the $[Ni(tacn)_3]^{3+}$ species. A spectrophotometric determination of $[Ni(tacn)_2^{2+}]$ at 799 nm (molar absorption coefficient = 7.41 $dm^3$ $mol^{-1}$ $cm^{-1}$) revealed that more than 96% of $[Ni(tacn)_2]^{3+}$ in the original solution was reduced to $[Ni(tacn)_2]^{2+}$ by $H_2O_2$. The observation that only 63% of the original $[Ni(tacn)_2]^{3+}$ was recovered by the re-oxidation of $Ni^{II}$ by peroxodisulfate (Fig. 1) may be attributed to the decomposition of $[Ni(tacn)_2]^{3+}$ during the oxidation by peroxodisulfate.[11] Therefore, it was concluded that the reduction of nickel(III) species by $H_2O_2$ occurs not at the ligand but at the metal center.

An attempt was made to determine the stoichiometry for the reaction of hydrogen peroxide with $[Fe(ttcn)_2]^{3+}$. The purity of $[Fe(ttcn)_2][ClO_4]_3$ was found spectrophotometrically to be 77.6% by dissolving the crystals in 2 mol $dm^{-3}$ $H_2SO_4$.[14] By using the same procedure applied to the reaction of hydrogen peroxide with $[Ni(tacn)_2]^{3+}$, the stoichiometry of this reaction was determined as 2.2:1 for $[Fe(ttcn)_2{}^{3+}]:[H_2O_2]$, which may be taken as 2:1, by considering the instability of $[Fe(ttcn)_2]^{3+}$ in solution.[14] All the reactions were observed at a constant ionic strength of $I = 0.10$ mol $dm^{-3}$ ($NaClO_4$).

## Results

### Oxidation of hydrogen peroxide by $[Ni(tacn)_2]^{3+}$

The reactions with excess amounts of hydrogen peroxide were excellently first order up to 4 half-lives. No rapid spectral change at the initial stage of the reaction was observed. The conditional second-order rate constant ($k = k_{obs}/[H_2O_2]_0$ where $[H_2O_2]_0$ is the total concentration of hydrogen peroxide) increased with decreasing hydrogen-ion concentration. This dependence of $k$ on $[H^+]$ indicates the following dual pathways for reaction (4) (M = Ni). As the resulting superoxide radical is

$$H_2O_2 \overset{K_a}{\rightleftharpoons} HO_2^- + H^+ \quad (1)$$

$$H_2O_2 + M^{3+} \xrightarrow{k_2} H_2O_2^{\bullet +} + M^{2+} \quad (5)$$

$$HO_2^- + M^{3+} \xrightarrow{k_1} HO_2^{\bullet} + M^{2+} \quad (6)$$

a moderately weak acid, $HO_2^{\bullet}$ is the predominant species under the experimental conditions.[6] Superoxide ions formed by reac-

$$HO_2^{\bullet} \rightleftharpoons O_2^{\bullet -} + H^+;\ pK_{a2} = 4.89 \quad (7)$$

tions (5) and (6) are then consumed either by reaction (9) with $Ni^{III}$ or by the disproportionation reaction (8).[5,6] In either case

$$2\ HO_2^{\bullet} \longrightarrow H_2O_2 + O_2 \quad (8)$$

$$HO_2^{\bullet} + M^{3+} \longrightarrow O_2 + M^{2+} + H^+ \quad (9)$$

the stoichiometry of the reaction is 2:1 as determined in this study. As the reactivity of superoxide radicals is very high, reactions (5) and (6) are the rate-determining steps and the rate law is given in equation (10). Plots of log $k$ *vs.* $-\log [H^+]$ gave

$$-\frac{d[M^{3+}]}{dt} = 2\left(\frac{k_1K_a}{[H^+]} + k_2\right)[H_2O_2][M^{3+}] \quad (10)$$

$$k_{obs} = 2\left(\frac{k_1K_a}{[H^+]} + k_2\right)[H_2O_2]_0 \quad (11)$$

straight lines with unit slope as shown in Fig. 2. Therefore, reaction (6) is the dominant process under the experimental conditions. Although an attempt was made to obtain the $k_2$ value by applying equation (10) for the results obtained at $[H^+] > 1 \times 10^{-3}$ mol $dm^{-3}$, the intercept of the plot of $k_{obs}$ *vs.* $[H^+]^{-1}$ was not meaningful within the experimental uncertainty $[(-4.83 \pm 3.19) \times 10^{-4}]$.

### Oxidation of hydrogen peroxide by $[Fe(ttcn)_2]^{3+}$ and $[Ru(bipy)_3]^{3+}$

As $[Fe(ttcn)_2]^{3+}$ decomposes at high pH, measurements were carried out under acidic conditions ($8.12 \times 10^{-3} < [H^+] < 3.05 \times 10^{-2}$ mol $dm^{-3}$), where the iron complex is stable for more than 30 min. As the range of hydrogen-ion concentration

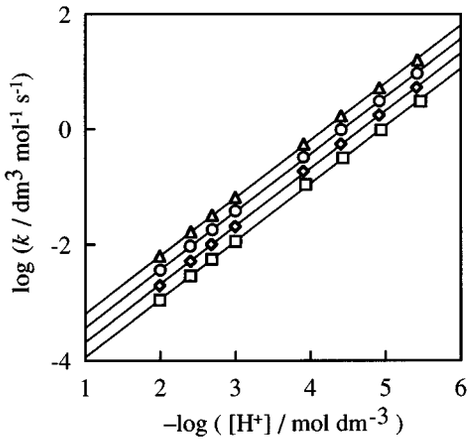



**Fig. 2** Plots of log $k$ *vs.* $-\log [H^+]$ for the reaction of $H_2O_2$ with $[Ni(tacn)_2]^{3+}$. The symbols represent the data obtained at 303.2(△), 298.2(○), 293.2(◇) and 288.8 K(□). $[Ni(tacn)_2{}^{3+}]_0 = (0.500–1.00) \times 10^{-4}$ mol $dm^{-3}$, $[H_2O_2] = 0.02–0.19$ mol $dm^{-3}$

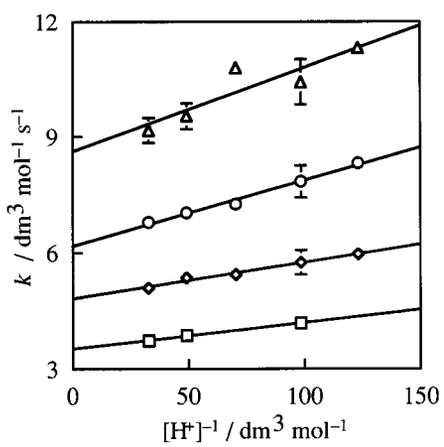



**Fig. 3** Plots of $k$ *vs.* $[H^+]^{-1}$ for the reaction of $H_2O_2$ with $[Fe(ttcn)_2]^{3+}$. Symbols as in Fig. 2. $[Fe(ttcn)_2{}^{3+}]_0 = 1.40 \times 10^{-3}$ mol $dm^{-3}$, $[H_2O_2] = 0.025–0.21$ mol $dm^{-3}$

was narrow, the conditional second-order rate constant ($k = k_{obs}/[H_2O_2]_0$) was plotted against $[H^+]^{-1}$ by assuming equations (10) and (11) for this reaction (Fig. 3). The linear dependence of $k$ on the reciprocal hydrogen-ion concentration indicates the dual pathways expressed by equations (5) and (6). The second-order rate constants, $k_1$ and $k_2$, corresponding to (5) and (6), are listed in Table 1, together with the activation parameters for each process.

The oxidation reaction of hydrogen peroxide by $[Ru(bipy)_3]^{3+}$ was observed at $3.91 < pH < 6.63$, to confirm the previous results reported by Macartney.[9] A plot of log $k$ ($k = k_{obs}/[H_2O_2]_0$) against $-\log[H^+]$ at 25 °C (Fig. 4) appears to be a straight line, indicating that reaction (6) is the dominant process. The solid line in Fig. 4 was obtained by non-linear least-squares analysis on the basis of equation (11). The obtained rate constants, $k_1$ and $k_2$, were $(3.70 \pm 0.26) \times 10^7$ and $3.57 \pm 1.19$ $dm^3$ $mol^{-1}$ $s^{-1}$, respectively. These results suggest that reaction (5) is negligibly slow compared with the $k_1$ process. A value of $3 \times 10^7$ $dm^3$ $mol^{-1}$ $s^{-1}$ was reported for $k_1$ in the previous study,[9] which seems in satisfactory agreement with the present value considering the difference in the experimental conditions: measurements in ref. 9 were made at $[LiCF_3SO_3] = 0.50$ mol $dm^{-3}$ while our measurements were carried out at $[NaClO_4] = 0.10$ mol $dm^{-3}$.

### Kinetic isotope effect for the oxidation of hydrogen peroxide by $[Ni(tacn)_2]^{3+}$

The conditional rate constant, $k_D$ ($= k_{obs}/[D_2O_2]_0$), was determined at various temperatures at the constant concentration of

**Table 1** Rate constants and activation parameters obtained for oxidation reactions of $H_2O_2$

| Oxidant | Rate constant*/dm$^3$ mol$^{-1}$ s$^{-1}$ | $\Delta H^{\ddagger}$/kJ mol$^{-1}$ | $\Delta S^{\ddagger}$/J K$^{-1}$ mol$^{-1}$ |
|---|---|---|---|
| $[Ni(tacn)_2]^{3+}$ | $k_1$ (6.15 ± 0.06) × 10$^6$ | 46.9 ± 0.4 | 42 ± 1 |
| $[Fe(ttcn)_2]^{3+}$ | $k_1$ (2.63 ± 0.18) × 10$^9$ | 26.7 ± 4.1 | 25 ± 14 |
| | $k_2$ 3.12 ± 0.03 | 40.1 ± 0.9 | −101 ± 3 |
| $[Ru(bipy)_3]^{3+}$ | $k_1$ (3.70 ± 0.26) × 10$^7$ | | |
| | $k_2$ 3.57 ± 1.19 | | |

* At 298.2 K.

**Table 2** Rate constants obtained for the oxidation reaction of $HO_2^-$ by $[Ni(tacn)_2]^{3+}$ at various temperatures in water and $D_2O$*

| Solvent | | 288.2 K | 293.2 K | 298.2 K | 303.2 K |
|---|---|---|---|---|---|
| water | $-\log(K_H/dm^3\ mol^{-1})$ | 11.73 | 11.62 | 11.52 | 11.42 |
| | $k_{1H}/10^6$ dm$^3$ mol$^{-1}$ s$^{-1}$ | 3.08 ± 0.28 | 4.35 ± 0.04 | 6.15 ± 0.06 | 8.49 ± 0.08 |
| $D_2O$ | $-\log(K_D/dm^3\ mol^{-1})$ | 12.37 | 12.16 | 12.26 | 12.06 |
| | $k_{1D}/10^6$ dm$^3$ mol$^{-1}$ s$^{-1}$ | 1.05 ± 0.04 | 1.56 ± 0.05 | 2.25 ± 0.06 | 3.21 ± 0.09 |

* The equilibrium constant, $K_D$, at 298.2 K was estimated from reported values of $K_H$ by using the following equation,[15] from the fourteen acid–base equilibria for which both $K_H$ and $K_D$ values have been reported, $\log(K_H/K_D) = C \log K_H$, where $C$ is a constant. The $K_D$ values at other temperatures were calculated by assuming that the reaction enthalpy is identical for $H_2O_2$ and $D_2O_2$.[16]

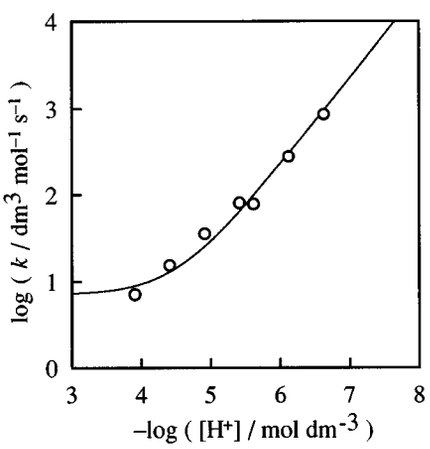



**Fig. 4** Plot of log $k$ *vs.* $-\log$ [H$^+$] for the reaction of $H_2O_2$ with $[Ru(bipy)_3]^{3+}$. The solid line is the best-fit curve estimated by the non-linear least-squares analysis on the basis of equation (11). $[Ru(bipy)_3^{3+}]_0 = 2.00 \times 10^{-5}$ mol dm$^{-3}$, $[H_2O_2]_0 = 0.0067$–$0.092$ mol dm$^{-3}$

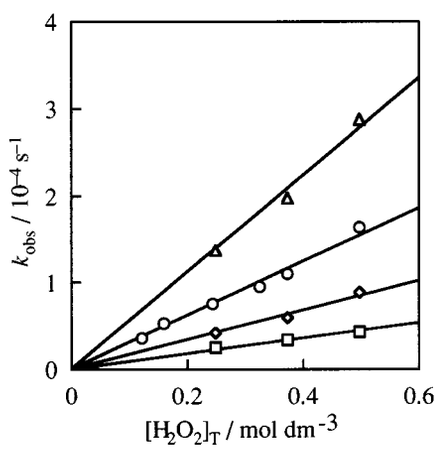



**Fig. 5** Plots of $k_{obs}$ *vs.* initial concentration of hydrogen peroxide in $D_2O$. [D$^+$] = 1.00 × 10$^{-2}$ mol dm$^{-3}$. $[H_2O_2]_T$ on the horizontal axis denotes the initial concentration of $H_2O_2$ dissolved in $D_2O$. Symbols as in Fig. 2

[D$^+$] = 1.00 × 10$^{-2}$ mol dm$^{-3}$ in $D_2O$. The results are shown in Fig. 5, and $k_D$ was (3.12 ± 0.08) × 10$^{-4}$ dm$^3$ mol$^{-1}$ s$^{-1}$ at 25 °C, which is significantly smaller than that obtained in water [(3.61 ± 0.03) × 10$^{-3}$ dm$^3$ mol$^{-1}$ s$^{-1}$]. On the basis of the treatment by Bell,[15] the $K_a$ value for $D_2O_2$ was estimated at 298.2 K. The values of $K_a$ in $D_2O$ at other temperatures were calculated by assuming that the enthalpy for reaction (3) is identical to that for (2).§ In Table 2 are listed the values of thus calculated $K_{aD}$ and $k_{1D}$ (the subscript D indicates that the values were obtained in $D_2O$ while $k_{1H} = k_1$). The net isotope effect, $k_{1H}/k_{1D}$, at 25 °C was 2.28 ± 0.05. The isotope effect for the pre-exponential factor $A_H/A_D$, expressed by equation (12), was

$$\ln(k_{1H}/k_{1D}) = \ln(A_H/A_D) + [(\Delta E_D - \Delta E_H)/RT] \qquad (12)$$

calculated as 2.2 ± 0.3, which is much larger than the limiting value of 0.7–1.4 expected for the existence of proton tunnelling;[16] here $\Delta E$ denotes the activation energy for the reactions in water and $D_2O$.

§ This assumption may not be valid for these reactions. However, the ratio of $A_H/A_D$ is not affected by this assumption, as the difference in the reaction free energies for equations (2) and (3) is attributed to the second term of the right-hand side of equation (12). A value of 2.2 ± 0.3 for $A_H/A_D$ estimated from $k_{1H}/k_{1D}$ is identical to that estimated from the gross rate constants, $k_H/k_D$.

## Discussion

Redox potentials for the reactions of $H_2O_2^{\bullet +}$–$H_2O_2$ and $HO_2^{\bullet}$–$HO_2^-$ couples are expressed by equations (13) and 14).[6,9]

$$HO_2^{\bullet} + H^+ + e^- \rightleftharpoons H_2O_2;\ E^o = 1.44\ V \qquad (13)$$

$$HO_2^{\bullet} + e^- \rightleftharpoons HO_2^-;\ E^o = 0.74\ V \qquad (14)$$

The relation between the rate constants for the cross-reaction and the self-exchange reactions can be described by the Ratner-type cross-relations (15)–(17), regardless of the reaction

$$k_{12} = (k_{11}k_{22}K_{12})^{\frac{1}{2}}W_{AB} \qquad (15)$$

$$W_{12} = \exp[-(w_{12} + w_{21} - w_{11} - w_{22})/2RT] \qquad (16)$$

$$w_{ij} = 4.225 \times 10^3\ z_i z_j/r(1 + 0.329\ r\ I^{\frac{1}{2}}) \qquad (17)$$

mechanism.[17,18] where $k_{11}$, $k_{22}$, $k_{12}$ and $K_{12}$ are the self-exchange rate constants, the rate constant for the cross-reaction, and the equilibrium constant of the cross-reaction, respectively; $z_i$, $z_j$, and $r$ are the ionic charges and the sum of the ionic radii of each reacting species. Equation (15) is valid for every type of reaction if the following two requirements are fulfilled:[17] (1) the activation process for each reactant is independent of the other reactant and (2) the activated species are the same for the self-exchange and cross-reaction.

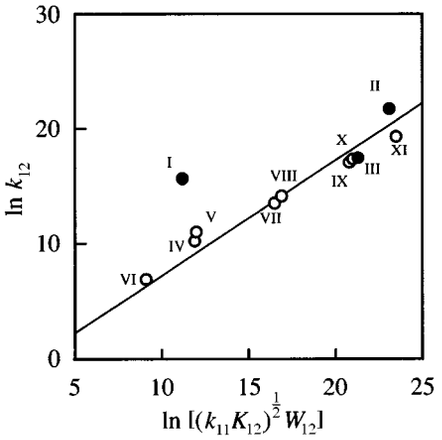
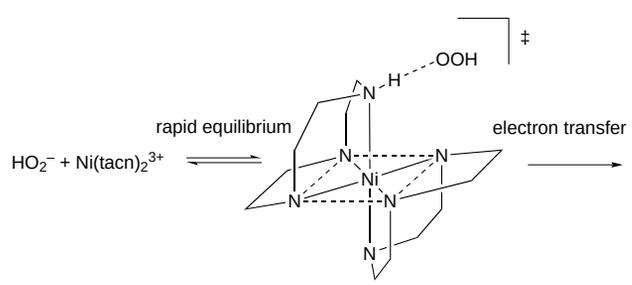



**Fig. 6** Plot of ln $k_{12}$ *vs.* ln$[(k_{11}K_{12})^{\frac{1}{2}}W_{12}]$ on the basis of equation (17). The Roman numbers denote that each circle represents the reaction of $HO_2^-$ with: $[Ni(tacn)_2]^{3+}$, **I**; $[Fe(ttcn)_2]^{3+}$, **II**; $[Ru(bipy)_3]^{3+}$ (this work), **III**; $[Os(dmbipy)_3]^{3+}$, **IV**; $[Os(bipy)_3]^{3+}$, **V**; $[Fe(dmbipy)_3]^{3+}$, **VI**; $[Fe(bipy)_3]^{3+}$, **VII**; $[Ru(dmbipy)_3]^{3+}$, **VIII**; $[Ru(bipy)_3]^{3+}$ (ref. 9), **IX**; $[Ni(dmbipy)_3]^{3+}$, **X**; $[Ni(bipy)_3]^{3+}$, **XI** (dmbipy = 4,4′-dimethyl-2,2′-bipyridine)




**Scheme 1**

In Fig. 6 a plot of ln $k_{12}$ *vs.* ln $[(k_{11}K_{12})^{\frac{1}{2}}W_{12}]$ is shown for the oxidations of $HO_2^-$ by various tris(polypyridine)metal(III) complexes in aqueous solution,[9] together with the results obtained in this study. All the reactions except the oxidation of $HO_2^-$ by $[Ni(tacn)_2]^{3+}$ fit on a straight line with unit slope. Therefore, it may be concluded that the oxidations of $HO_2^-$ by $[Fe(ttcn)_2]^{3+}$ and $[Ru(bipy)_3]^{3+}$, and those by **IV–XI**, proceed through an outer-sphere mechanism.[9] On the other hand, the rate constant for the oxidation of $HO_2^-$ by $[Ni(tacn)_2]^{3+}$ ion is much larger than that predicted by the outer-sphere reactions. In such a case a specific interaction between $HO_2^-$ and the amino proton on the tacn ligand may be indicated.[19] The involvement of the amino proton is supported by the fact that the oxidation of $HO_2^-$ by $[Fe(ttcn)_2]^{3+}$, which has a similar structure to that of $[Ni(tacn)_2]^{3+}$ with no reactive (or labile) hydrogen atom, occurs *via* the outer-sphere mechanism.

deMaine and Stanbury reported that the reaction of $[Ni(tacn)_2]^{3+}$ with NO involved N-deprotonated $[Ni^{III}(tacn)(tacn - H)]^{2+}$ species and did not produce $[Ni(tacn)_2]^{2+}$ {$[Ni^{III}(tacn)(tacn - H)]^{2+}$ represents the N-deprotonated conjugate base form of $[Ni(tacn)_2]^{3+}$}. A p$K_a$ value for the deprotonation of the co-ordinated tacn was estimated as *ca.* 11.[20] Therefore, the degree of deprotonation of the co-ordinated tacn ligand should be very small under the experimental conditions. Moreover, the stoichiometric yield of $[Ni(tacn)_2]^{2+}$ observed in this study (Fig. 1) indicates that such a species suggested by deMaine and Stanbury was not involved in the reaction of $[Ni(tacn)_2]^{3+}$ with $HO_2^-$. Instead, the kinetic isotope effect observed for the oxidation of $HO_2^-$ by $[Ni(tacn)_2]^{3+}$ strongly indicates an interaction between the amino proton on the tacn ligand and $HO_2^-$ during the activation process (Scheme 1). The relatively small value of $k_{1H}/k_{1D}$(= 2.28 ± 0.05 at 25 °C) indicates that this interaction may not lead to a proton-transfer reaction or that the transfer of a proton in the transition state occurs to a much lower extent compared with the 50% transfer assumed for the maximum isotope effect ($k_{1H}/k_{1D} = 8$).[16,19] As the proton exchange on the amino nitrogen atom of tacn is reported to be very fast,[11] it is possible to consider that electron transfer takes place coupled with a proton-transfer reaction, followed by rapid protonation of the amino nitrogen atom. Therefore the mechanism in equations (18)–(20) similar to that

$$[Ni^{III}(tacn)_2]^{3+} + HO_2^- \overset{K'}{\rightleftharpoons} [Ni^{III}(tacn)(tacn{-}O_2H)^{2+}]^* \quad (18)$$

$$[Ni^{III}(tacn)(tacn{-}O_2H)^{2+}]^* \xrightarrow{k} [Ni^{II}(tacn)(tacn - H)]^+ + H^+ + HO_2^\bullet \quad (19a)$$

$$\text{or } [Ni(tacn)_2]^{2+} + HO_2^\bullet \quad (19b)$$

$$[Ni(tacn)(tacn - H)]^+ + H^+ \xrightarrow{\text{fast}} [Ni(tacn)_2]^{2+} \quad (20)$$

$$[Ni(tacn)_2]^{3+} + HO_2^\bullet \xrightarrow{\text{fast}} [Ni(tacn)_2]^{2+} + O_2 + H^+ \quad (21)$$

for the reaction of $[Co(sep)]^{2+}$ (sep = sepulchrate,1,3,6,8,10,-13,16,19-octaazabicyclo[6.6.6]eicosane) with $O_2^{\bullet -}$ is suggested for the oxidation of $HO_2^-$ by $[Ni(tacn)_2]^{3+}$,[19] where $[Ni^{III}(tacn)(tacn{-}O_2H)^{2+}]^*$ is the species shown in Scheme 1, and the species $[Ni^{II}(tacn)(tacn - H)]^+$ is the N-deprotonated conjugate base form of $[Ni(tacn)_2]^{2+}$. If $K'$ is not very large ($\ll 10^6$ dm$^3$ mol$^{-1}$), the rate law can be expressed by equation (10) with $k_1 = kK'$. It seems reasonable to assume that $K'$ is smaller than $10^6$, considering that the maximum value for an outer-sphere association constant is 5 dm$^3$ mol$^{-1}$ for $[Ni(tacn)_2]^{3+}$ and $HO_2^-$ under the experimental conditions.[21] However, the possibility of other proton-mediated mechanisms, such as the double exchange or superexchange-type mechanism,[22] may not be ruled out, as the ratio of the pre-exponential factors ($A_H/A_D$) indicates no proton tunnelling expected for the ordinary proton-transfer reactions.[16]

From the intercept of the plot in Fig. 6, a value of $(3.8 \pm 0.3) \times 10^{-3}$ dm$^3$ mol$^{-1}$ s$^{-1}$ was calculated as the electron self-exchange rate constant of the $HO_2^\bullet$–$HO_2^-$ couple, $k_{ex}(HO_2^\bullet{-}HO_2^-)$, which is consistent with the value reported by Macartney.[9] Eriksen *et al.*[23] reported the reaction of $ClO_2^\bullet$ with $HO_2^-$. From their results, $3 \times 10^4$ dm$^3$ mol$^{-1}$ s$^{-1}$ was calculated as $k_{ex}(HO_2^\bullet{-}HO_2^\bullet)$, which is about $10^7$ times larger than $(3.8 \pm 0.3) \times 10^{-3}$ dm$^3$ mol$^{-1}$ s$^{-1}$ estimated here. It may be reasonable to consider that the reaction studied by Eriksen *et al.* may not proceed through the simple outer-sphere mechanism. For the electron-transfer reactions between small molecules such as those of $HO_2^-$ and $ClO_2^\bullet$, a specific intermediate (or a precursor complex) which causes strong interaction between the electronic orbitals of the reactants has been proposed.[24,25] Unlike the oxidation of $HO_2^-$ by $[Ni(tacn)_2]^{3+}$, a strong acid–base interaction between $HO_2^-$ and $ClO_2^\bullet$ takes place as the anion affinity of $ClO_2^\bullet$ is very large.[23] Therefore, the oxidation of $HO_2^-$ by $ClO_2^\bullet$ probably occurs, with a somewhat inner-sphere character, through strong electronic coupling caused by the acid–base (donor–acceptor) interaction between these two molecules in the transition state.

For reactions involving small molecules such as the $O_2$–$O_2^{\bullet -}$ couple, strong solvation of anions was suggested to explain the relatively slow self-exchange rate constants.[17] The small rate constant of the outer-sphere electron-exchange reaction for the $HO_2^\bullet$–$HO_2^-$ couple may also be attributed to the strong solvational interaction for $HO_2^-$. Macartney[9] tried to explain the slow electron-exchange rate constant for this couple on the basis of a semiclassical model. His calculation using the hard-sphere radii of $HO_2^-$ and $HO_2^\bullet$ species yielded a *ca.* $10^2$ times larger value for the self-exchange rate constant than the

experimentally obtained value. The application of semiclassical theory to the electron-exchange reactions of the $ClO_2^{\bullet}$–$ClO_2^-$ and $NO_2^{\bullet}$–$NO_2^-$ couples[26,27] led to the conclusion that the calculated interaction distances between each redox pair were *ca*. 100 pm larger than the sum of the hard-sphere radii of each species,[9] which suggests that electron-transfer reactions involving small ions take place through the solvational sheath around the ions. On this basis, the relative slowness of the electron transfer for the $HO_2^{\bullet}$–$HO_2^-$ couple may be explained by the non-adiabatic effect originating from the lower electronic interaction between the reactants. The relations have been derived from the semiclassical treatment for the non-adiabatic electron-transfer reactions,[28,29] where $\kappa_{el}$ and $\nu_n$ are the electronic transmission

$$k = \nu_{el}\exp[(\Delta G_{OS}^* + \Delta G_{IS}^*)/RT] \quad (22)$$

$$\kappa_{el} = 2[1 - \exp(-\nu_{el}/2\nu_n)]/[2 - \exp(\nu_{el}/2\nu_n)] \quad (23)$$

$$\nu_{el} = (H_{AB}^2/h)(\pi^3/RT\Delta G_{OS}^*)^{\frac{1}{2}} \quad (24)$$

$$H_{AB} = H_{AB}^0\exp[-\alpha(\sigma - \sigma_0)] \quad (25)$$

coefficient and the nuclear frequency, $H_{AB}$ and $H_{AB}^0$ are the electronic coupling factors for the non-adiabatic and adiabatic cases, $\alpha$, $\sigma$ and $\sigma_0$ are the distance scaling factor and the separations between the reactants for the non-adiabatic and adiabatic cases, and $\Delta G_{OS}^*$ and $\Delta G_{IS}^*$ denote the outer- and inner-sphere reorganization free energies, respectively. As the electronic coupling factor decreases exponentially with increasing distance between the reactants [equation (25)], the separation of two reactants by the solvation sheath significantly reduces the rate of the electron-transfer reaction.

By assuming the p$K_a$ value for reaction (1) is 1.0,[8a] the electron self-exchange rate constant for the $H_2O_2^{\bullet+}$–$H_2O_2$ couple was calculated as $3 \times 10^{-7}$ dm$^3$ mol$^{-1}$ s$^{-1}$ from the cross-reaction with $[Fe(ttcn)_2]^{3+}$. The self-exchange rate constant for this couple was estimated as $2.5 \times 10^{-9}$ dm$^3$ mol$^{-1}$ s$^{-1}$ from the reaction of $H_2O_2$ with $[Ni(bipy)]^{3+}$ reported by Wells and Fox.[5] These two self-exchange rate constants may be in good agreement with each other, considering the accuracy of the calculation and the difference in the experimental conditions.[5] However, the self-exchange rate constant for the $H_2O_2^{\bullet+}$–$H_2O_2$ couple is more than $10^4$ times smaller than that for the $HO_2^{\bullet}$–$HO_2^-$ couple. The very small self-exchange rate constant for the $H_2O^{\bullet+}$–$H_2O_2$ couple cannot be explained by the difference in the thickness of the solvational sheaths of these ions as the solvation of the $HO_2^-$ ion is supposed to be greater compared with that of $H_2O_2^{\bullet+}$ in water.[30] Moreover, the estimated inner-sphere contribution to the activation free energy for the $H_2O_2^{\bullet+}$–$H_2O_2$ couple is almost identical to that for the $HO_2^{\bullet}$–$HO_2^-$ couple.[9,17] Therefore, it may be assumed that the self-exchange rate constant for the $H_2O_2^{\bullet+}$–$H_2O_2$ couple is comparable to or faster than that for the $HO_2^{\bullet}$–$HO_2^-$ couple.[9] In such a case, a maximum value of $-4.8$ was estimated as the p$K_a$ value for reaction (1) from the relation given in equation (15). Kustin and coworkers[8a] used 1.0 as the p$K_a$ value for reaction (1) for the analysis of the reaction of $H_2O_2$ with $Mn^{III}$. More recently, Schwarz[8b] argued that the p$K_a$ value for reaction (1) should be less than $-10$ and that $H_2O_2^{\bullet+}$ is an unlikely participant in reactions in water considering the stability of $H_3O_2^+$. The value of p$K_a < -4.8$ for reaction (1) estimated in this study is, therefore, closer to that postulated by Schwarz, and this result supports the involvement of the solvational sheath in the electron-transfer reactions of small ions or molecules such as hydrogen peroxide.

## Conclusion

It may be summarized that the redox reactions involving $HO_2^-$ proceed in the following three ways: (1) an outer-sphere mechanism with inert metal complexes (however, the reactions may be non-adiabatic), (2) electron transfer coupled with proton transfer or through the double exchange/superexchange-type interaction, and (3) strong electronic coupling by direct donor–acceptor interaction between the reacting species.

The slow electron-transfer rate constants for the reactions involving small ions may be explained by the non-adiabatic effect originating from the strong solvation of these small ions. Such speculation was also made previously by Jordan and Macartney.[9,17] A maximum value of $-4.8$ was estimated as the p$K_a$ value for reaction (1) from the limiting self-exchange rate constant for the $H_2O^{\bullet+}$–$H_2O_2$ couple.

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