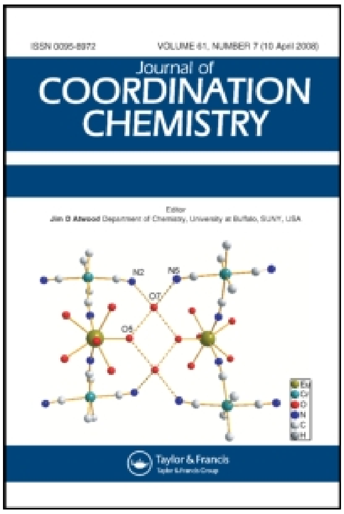

Journal of Coordination Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713455674

METAL IONS AND HYDROGEN PEROXIDE XXIX. On the Kinetics and Mechanism of the Catalase-like Activity of Nickel(II) and Nickel(II)-Amine Complexes

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To cite this Article Sigel, Helmut , Wyss, Kurt , Waldmeier, Peter and Griesser, Rolf(1974) 'METAL IONS AND HYDROGEN PEROXIDE XXIX. On the Kinetics and Mechanism of the Catalase-like Activity of Nickel(II) and Nickel(II)-Amine Complexes', Journal of Coordination Chemistry, 3: 3, 235 — 247

To link to this Article: DOI: 10.1080/00958977408073818

URL: http://dx.doi.org/10.1080/00958977408073818

J. Coord. Chem.
Vol. 3, pp. 235 247

METAL IONS AND HYDROGEN PEROXIDE
XXIX. On the Kinetics and Mechanism of the Catalase-like Activity of Nickel(II) and Nickel(II)-Amine Complexes[1]

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(Received February 13th, 1973; in final form December 4th, 1973)

The disproportionation of H_2O_2, catalyzed by Ni^{2+}_{aq} and several Ni^{2+}-amine complexes, was investigated. (i) With Ni^{2+}_{aq} in the pH range 6.6–8.2 and without buffer the following rate law holds: $\nu_0 = d[O_2]/dt = k[Ni^{2+}][H_2O_2]^2/[H^+]$ ($k = (1.77 \pm 0.23) \times 10^{-9}$ mol^{-1} l. sec^{-1}). In the presence of phosphate buffer and in the pH range 6–7 the initial rate, ν_0, is proportional to $1/[H^+]$. (ii) For the buffer-free Ni^{2+}-2,2′-bipyridyl 1:1 system in the pH range 4.5–8 $\nu_0 = ((k_1/[H^+]) + k_2)[H_2O_2]([Ni^{2+}]_{tot} = [Bipy]_{tot})^{0.5}$ where $k_1 = (1.35 \pm 0.20) \times 10^{-12}$ mol$^{0.5}$ l.$^{-0.5}$ sec^{-1} and $k_2 = (2.5 \pm 0.5) \times 10^{-6}$ mol$^{-0.5}$ l.$^{0.5}$ sec^{-1}. With borate buffer ν_0 is increased, but in the pH-dependent part the given proportionalities between ν_0 and [reactants] are valid. For these conditions the Ni^{2+}-2,2′-bipyridyl 1:1 complex is the catalytically most active species. (iii) In the buffer-free system with $Ni(ethylenediamine)_2^{2+}$ as catalyst in the pH range 8.2–10 it appears that an analog rate law holds as given above for Ni^{2+}_{aq} (*cf.* i). Borate buffer has a rate enhancing effect on the catalytic activity of $Ni(En)_2^{2+}$ Also there is evidence for ν_0 being proportional to $1/[H^+]^2$ and this means two HOO^- (or corresponding borate derivatives) are participating in the reaction before the rate determining step. (iv) With 2-picolylamine the 1:1 complex reaches about the activity of Ni^{2+}, while with 4-aminomethylimidazole or histamine none of the complex species is as active as Ni^{2+}. – As far as possible the reaction laws are given for the mentioned systems. Reaction mechanisms and the structure of the active species, as well as the rate enhancing effect of borate, are discussed.

INTRODUCTION

Among the complexes of metal ions of the first transition series which catalyze in homogenous phase the disproportionation of H_2O_2, (reaction 1), com-

$$2H_2O_2 \longrightarrow O_2 + 2H_2O \qquad (1)$$

plexes of iron[2, 3] and copper[4] are most extensively studied. This is probably due to the presence of these two metal ions in redox-active enzyme systems occurring in nature.

A suitable catalyst for reaction 1 has to have at least the following three distinct qualities:[5] (i) The metal ion has to be redox active; *i.e.*, there must be two or more different oxidation states. (ii) "Free" coordination positions must be available; *i.e.*, peroxo species must be able to coordinate. (iii) The coordination sphere of the metal ion must be "labile"; *i.e.*, sufficiently high exchange rates are necessary that a catalyst may be effective.

Next, the catalase-like activity of a free (hydrated) metal ion with one of its complexes has to be compared. Even though the mentioned iron- and copper-complexes are among the most effective catalysts,[3,5] the activity of the corresponding "free" metal ions is difficult to study due to their large tendency for hydrolysis. However, nickel(II) is stable towards hydrolysis up to a pH of approximately 8,[6] and thus is suitable for such a study, although it is not a very powerful catalyst (in accord with its low redox activity).[7] To elucidate also the influence of ligands and to see if different reaction paths are used by the metal ion and its complexes, the Ni^{2+} systems containing 2, 2′-bipyridyl, ethylenediamine, 2-picolylamine, 4-aminomethylimidazole or histamine have been included. Additionally, as far as possible the influence of buffers ($[Na^+] = 0.1$; 25° C) on the reaction rate as well as on the kinetics was demonstrated.

EXPERIMENTAL SECTION

Materials

Ethylenediamine, 2,2′-bipyridyl, $Ni(ClO_4)_2 \cdot 6\,H_2O$, and $NaClO_4$ were obtained from Fluka AG, Buchs, Switzerland. H_2O_2 *pro analysi*, $TiOSO_4$, $KHSO_4$, H_3BO_3, Na_2HPO_4, $HClO_4$, and NaOH were from Merck AG, Darmstadt, Germany. α-Picolylamine

(2-amino-methylpyridine) was from Dr. F. Raschig GmbH, Ludwigshafen, Germany, and 4-aminomethylimidazole was the same as described recently.[8]

Measurements

The concentration of O_2 (the vessel was closed with a capillary) was determined with a Beckman Fieldlab TM Oxygen Analyzer connected with a Walz and Walz Recorder (Model 2011) or with an oxygraph of Gilson Medical Electronics, Middleton (Wisconsin, U.S.A.) equipped with a Beckman–Clark electrode. The recorders were calibrated using O_2-free water and water saturated with air. In the latter case $[O_2]$ = 4.55×10^{-4} M, 3.95×10^{-4}, 3.51×10^{-4}, 3.14×10^{-4}, 2.58×10^{-4}, 2.35×10^{-4}, 2.19×10^{-4}, and 2.0×10^{-4} at 0°, 5°, 10°, 15°, 25°, 30°, 35°, and 45° C, respectively.[9] The other apparatus and the determination of the concentrations of the H_2O_2 stock solutions were described recently,[5] as well as the experiments in the presence of buffer. Where no buffer was used the pH was adjusted with concentrated NaOH or $HClO_4$: as the pH was not stable, parallel experiments were carried out under exactly the same conditions: in one the $[O_2]$ was measured and in the other the pH. In this way to each initial rate, ν_0, the initial pH, *i.e.* $pH_{(t=0)}$, could be determined. In Figure 1 a typical pair of experiments is shown together with their evaluation.[5] The exact concentrations of all reagents are given in the legends to the figures.

RESULTS

1. The Hydrated Ni^{2+} as a Catalyst

1.1. The Ni^{2+}_{aq} system without buffers In the catalysis of the decomposition of H_2O_2 (reaction 1) the initial rate of the O_2 evolution, $\nu_0 = d[O_2]/dt$ (mol $l.^{-1}$ sec^{-1}), is proportional to $[H^+]^{-1}$, to $[H_2O_2]^2$ (*cf.* Fig. 2), and to $[Ni^{2+}]$ (varied from 5×10^{-4} M to 8×10^{-3} M). This is summarized in the rate law 2, where $k = (1.77 \pm 0.23) \times 10^{-9}$ mol^{-1}

$$\nu_0 = \frac{d[O_2]}{dt} = k\,\frac{[Ni^{2+}][H_2O_2]^2}{[H^+]} \tag{2}$$

l. sec^{-1}.[10] The activation energy, determined in the temperature range of 0° through 45°C ($[H_2O_2]_{tot(t=0)} 5 \times 10^{-2}$ M, $[Ni^{2+}] = 2 \times 10^{-3}$ M), is ΔE = 11.4 kCal mol^{-1}.

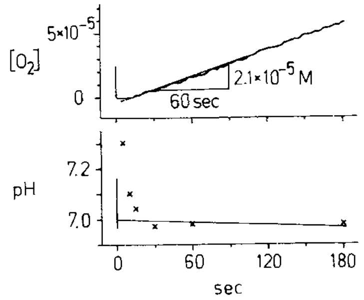


FIGURE 1 Example of a pair of measurements: (a) Evolution of O_2 from H_2O_2 (10^{-1} M) by Ni^{2+}_{aq} (2×10^{-3} M); I = 0.1 ($NaClO_4$); 25°C. Initial rate, $\nu_0 = d[O_2]/dt = 2.1 \times 10^{-5}/60 = 3.5 \times 10^{-7}$ mol $l.^{-1}$ sec^{-1}, *i.e.* $\log \nu_0 = -6.46$. (b) Determination of the initial pH under the above conditions: $pH_{(t=0)} = 7.00$. The solution containing all reagents except H_2O_2 had been adjusted to pH 7.81.

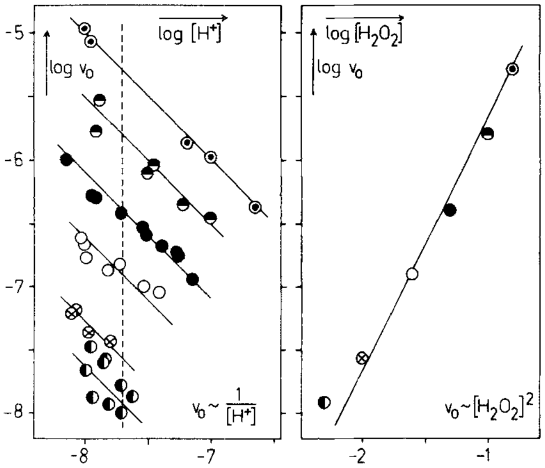


FIGURE 2 (a) Catalase-like activity of Ni^{2+}_{aq} (2×10^{-3} M) at different $[H_2O_2]_{tot(t=0)}$ (⊙, 1.6×10^{-1} M; ◓, 10^{-1} M; ●, 5×10^{-2} M; ○, 2.5×10^{-2} M; ⊗, 10^{-2} M; ◐, 5×10^{-3} M) in dependence on pH; I = 0.1 ($NaClO_4$); 25° C. (b) Evaluation of Figure 2a at pH 7.7.

1.2. The catalase-like activity of Ni^{2+} in the presence of buffers As Ni^{2+}-phosphate complexes are known to exist,[11] we expected an inhibition of the activity by the presence of phosphate buffer, so $[PO_4{}^{3-}]_{tot}$ was varied from zero to 10^{-1} M. Surprisingly, the activity in all these cases (where $[Ni^{2+}] = 2 \times 10^{-3}$ M and $[H_2O_2]_{tot(t=0)} = 5 \times 10^{-2}$ M) is about the same. However, reasonably accurate measurements could only be carried out in the pH range 6 to 7, where ν_0 is proportional to $[H^+]^{-1}$. In the pH range 7 to 7.5 remarkable deviations occur and at pH > 7.5 precipitates are formed.[12] Studies in borate buffer failed due to precipitation.

2. *The Ni^{2+}-2,2'-bipyridyl system as a catalyst*

2.1. *The Ni^{2+}-2,2'-bipyridyl system without buffers*

In Figure 3 the logarithm of v_0 is plotted *versus* log $[H^+]$. The dependence between v_0 and $[H^+]$ suggests that at pH $\geqslant 7.5$ v_0 is proportional to $[H^+]^{-1}$ and at pH $\leqslant 5$ v_0 is independent of $[H^+]$ while v_0 is always proportional to $[H_2O_2]$. The latter is still true at the highest possible concentrations of the catalyst ($([Ni^{2+}]_{tot} = [Bipy]_{tot} = 4 \times 10^{-3}$ M; $[Ni(Bipy)] = 1.48 \times 10^{-3}$ M)[13] and low initial concentrations of $[H_2O_2]_{tot(t=0)}$ (10^{-3} M to 1.6×10^{-2} M.[14] Additionally, v_0 is proportional to $([Ni^{2+}]_{tot} = [Bipy]_{tot})^{0.5}$ (Fig. 4).[15] An attempt to vary the ratio of $[Ni^{2+}]_{tot}$: $[Bipy]_{tot}$ failed due to precipitation. Hence, for reasons of analogy with the results obtained in buffer (*cf.* Section 2.2.), we can only assume that $Ni(Bipy)^{2+}$ and not $Ni(Bipy)_2{}^{2+}$ is the most active species.[16]

The results can be summarized in eq. 3, where k_1 =

$$v_0 = \frac{d[O_2]}{dt} = k_1 \frac{[H_2O_2]}{[H^+]}([Ni^{2+}]_{tot} = [Bipy]_{tot})^{0.5} + k_2[H_2O_2]([Ni^{2+}]_{tot} = [Bipy]_{tot})^{0.5} = \left(\frac{k_1}{[H^+]} + k_2\right)[H_2O_2]([Ni^{2+}]_{tot} = [Bipy]_{tot})^{0.5} \qquad (3)$$

$(1.35 \pm 0.20) \times 10^{-12}$ $mol^{0.5}$ $l^{-0.5}$ sec^{-1} and $k_2 = (2.5 \pm 0.5) \times 10^{-6}$ $mol^{-0.5}$ $l^{0.5}$ sec^{-1},[10] calculated with the data obtained for pH $\geqslant 7.5$ and pH $\geqslant 5.0$, respectively. Now, v_0 can be calculated (*cf.* the small empty points in Fig. 3), and there is a good agreement between the calculated and measured data.

The activation energy, ΔE, for this system ($[Ni^{2+}]_{tot} = [Bipy]_{tot} = 10^{-3}$ M; $[H_2O_2]_{tot(t=0)} = 10^{-1}$ M) was determined in the temperature range of 5° through 45° C. For the pH-dependent part of the reaction follows: ΔE = 20.5 Kcal mol^{-1}; for the pH-independent reaction ΔE is also not significantly different.

2.2. *The Ni^{2+}-2,2'-bipyridyl system with borate buffer*

First, experiments were carried out with constand $[H_2O_2]_{tot(t=0)}$, pH and $[Ni^{2+}]_{tot}$, but different $[2,2'\text{-bipyridyl}]_{tot}$. The results (Fig. 5)[13,17] indicate clearly that the most active species is the 2,2'-bipyridyl-Ni^{2+} 1:1 complex. The data, given in Figure 6,[18,19] show that at pH < 7.7 v_0 is proportional to $1/[H^+]$, while at higher pH values the reaction rate becomes more and more independent of the pH. Allover v_0 is proportional to $[Ni(Bipy)^{2+}]^{0.5}$; this and the dependence of v_0 on $[H_2O_2]$ is presented in Figure 7. The slope of the curves obtained by plotting log v_0 versus log $[H_2O_2]_{tot(t=0)}$ proceeds from 1 to <1, indicating saturation of the catalyst. As in the unbuffered system, even at small ratios of $[H_2O_2]_{tot(t=0)}$: [catalyst], no deviation from a slope of 1 is observed.

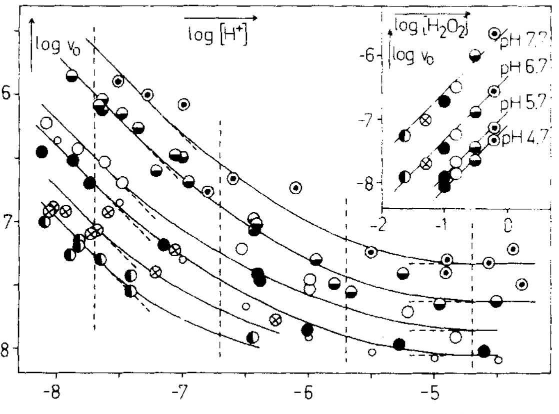


FIGURE 3 Catalase-like activity of the Ni^{2+}-2,2'-bipyridyl 1:1 system ($[Ni^{2+}]_{tot} = [Bipy]_{tot} = 10^{-3}$ M; $[Ni(Bipy)] = 3.71 \times 10^{-4}$ M, $[Ni^{2+}] = 3.45 \times 10^{-4}$ M, $[Ni(Bipy)_2] = 2.24 \times 10^{-4}$ M, $[Ni(Bipy)_3] = 6.0 \times 10^{-5}$ M)[13] at different $[H_2O_2]_{tot(t=0)}$ (⊙, 6×10^{-1} M; ◒, 3×10^{-1} M; ○, 1.5×10^{-1} M; ●, 10^{-1} M; ×, 5×10^{-2} M; ◐, 2.5×10^{-2} M) in dependence on pH; I = 0.1 ($NaClO_4$); 25° C. – (○) *calculated* with eq. 3 for the conditions of ●. *Inserted figure:* Evaluations at pH 4.7, 5.7, 6.7, and 7.7: $r_0 \sim [H_2O_2]$.

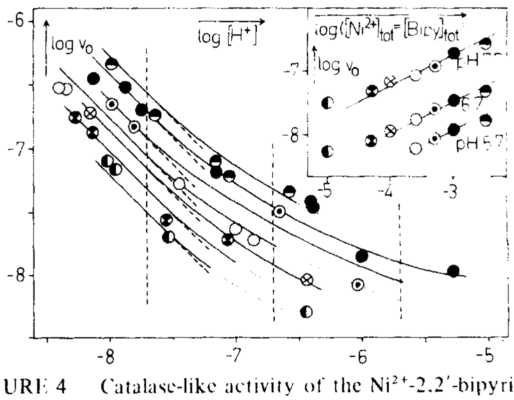


FIGURE 4 Catalase-like activity of the Ni^{2+}-2,2'-bipyridyl 1:1 system at $[H_2O_2]_{tot(t=0)} = 10^{-1}$ M and different concentrations of catalyst ($[Ni^{2+}]_{tot} = [Bipy]_{tot}$: ◓, 2×10^{-3} M; ●, 10^{-3} M; ⊙, 5×10^{-4} M; ○, 2.5×10^{-4} M; ⊗, 10^{-4} M; ⊗, 5×10^{-5} M; ◐, 10^{-5} M; Ni(Bipy) 37.06%, $Ni^{2+} \leqslant 34.8\%$, $Ni(Bipy)_2 \leqslant 22.4\%$, $Ni(Bipy)_3 \leqslant 6.1\%$)[13] in dependence of pH; I = 0.1 ($NaClO_4$); 25° C. The dotted lines are tentatively extended. *Inserted figure*: Evaluations at pH 5.7, 6.7, and 7.7: $r_0 \sim ([Ni^{2+}]_{tot} = [Bipy]_{tot})^{0.5}$.

i.e., there is again no hint for a higher order dependency between v_0 and $[H_2O_2]$. These results indicate that in the active species HOO^- is co-ordinated. Hence, principally the same kinetic parameters are observed in borate and in the buffer-free system with two slight differences: (i) In the buffer-free system saturation of the catalyst is not reached. (ii) In borate buffer no pH-independent reaction is found in the pH range studied.

The experiments given as an insertion in Figure 6 show that at $[H_3BO_3]_{tot} < 10^{-2}$ M the measured v_0 is identical with the one of the unbuffered system. However, with increasing concentrations of borate v_0 *increases* too unitl with 0.5 M solutions saturation is reached. This rate of enhancing effect can only mean that borate, or derivatives thereof, participate in the catalysis.

The activation energy for the activity ($[H_2O_2]_{tot(t=0)}$ = 1.25 x 10^{-2} M) of $Ni(Bipy)^{2+}$ ($[Ni^{2+}]_{tot}$ = $[Bipy]_{tot}$ = 10^{-3} M) in the presence of 0.1 M borate buffer at pH 8.30 was determined in the temperature range of 5° through 45° C: ΔE = 17.9 Kcal mol^{-1}.

2.3. The Ni^{2+}-2,2′-bipyridyl system in the presence of phosphate buffer It appears that in certain pH regions phosphate has a slight increasing effect on the reaction rate (Fig. 8), but no unequivocal statement can be made. However, another feature is definite: As in the buffer-free system at lower pH values, v_0 is independent of $[H^+]$; then the rate increases with increasing pH and becomes again independent of pH, thus indicating saturation, This is evidence for the participation of H_2O_2 at lower pH values and of HOO^- at higher pH values in the reaction process.

3. The Ni^{2+}-Ethylenediamine System as a Catalyst

3.1 The Ni^{2+}-ethylenediamine system without buffers As usual, first we studied the background catalysis of the disproportionation of H_2O_2, *i.e.* reaction mixtures containing all reactants except Ni^{2+} were tested. It was in the order of the reaction rate in the presence of the Ni^{2+}-ethylenediamine 1:2 complex,[20] even though great care was taken to exclude impurities.[21] Hence, only tentative conclusions could be drawn. The results (for pH 8.2 to 10) are summarized in eq. 4, where the estimated rate constant, k =

$$v_0 = \frac{d[O_2]}{dt} = k\,\frac{[Ni(En)_2{}^{2+}]\,[H_2O_2]^2}{[H^+]} \qquad (4)$$

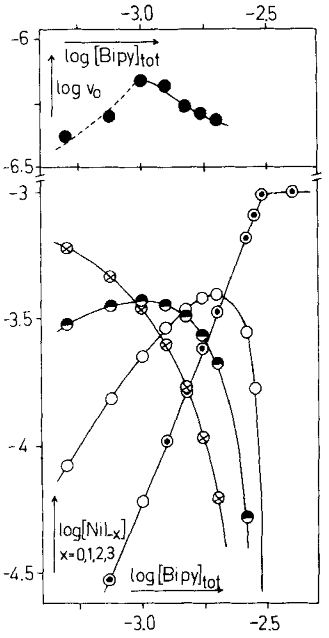


FIGURE 5 Catalase-like activity of Ni^{2+}-2,2′-bipyridyl. *Upper part:* Dependence on $[2,2'\text{-bipyridyl}]_{tot}$ at $[Ni^{2+}]_{tot}$ = 10^{-3} M, $[H_2O_2]_{tot(t=0)}$ = 1.25 x 10^{-2} M, and pH 9.36 ($[borate]_{tot}$ = 0.1 M); $[Na^+]_{tot}$ = 0.1 M; 25°C. The dashed line indicates uncertainty due to a possible precipitation. The *lower part* shows the distribution of the several species[13] under the above conditions[17] in their dependence on $[2,2'\text{-bipyridyl}]_{tot}$: Ni^{2+} (⊗), $Ni(Bipy)^{2+}$ (◓), $Ni(Bipy)_2{}^{2+}$ (○), and $Ni(Bipy)_3{}^{2+}$ (⊙).

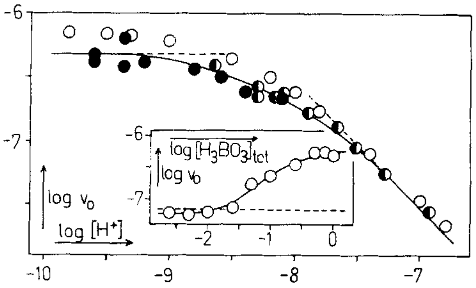


FIGURE 6 Catalase-like activity of $Ni(Bipy)^{2+}$ ($[Ni^{2+}]_{tot}$ = $[Bipy]_{tot}$ = 10^{-3} M; $[Ni(Bipy)]$ = 3.71 x 10^{-4} M, $[Ni^{2+}]$ = 3.45 x 10^{-4} M, $[Ni(Bipy)_2]$ = 2.24 x 10^{-4} M, $[Ni(Bipy)_3]$ = 6.0 x 10^{-5} M)[13,17] in dependence on pH (●, ◐).[18,19] $[H_2O_2]_{tot(t=0)}$ = 1.25 x 10^{-2} M; $[borate]_{tot}$ = 0.1 M; $[Na^+]_{tot}$ = 0.1 M; 25°C. – *Calculated* v_0 (*cf.* eq. 12; k_3 = 3.82 x 10^{-5} $mol^{0.5}$ $l.^{-0.5}$ sec^{-1}, K_M = 4.02 x 10^{-6} mol $l.^{-1}$) for the above conditions: (○). – *Inserted figure:* Activity of $Ni(Bipy)^{2+}$ ($[Ni^{2+}]_{tot}$ = $[Bipy]_{tot}$ = 10^{-3} M) in dependence on $[borate]_{tot}$ at pH 8.10. $[H_2O_2]_{tot(t=0)}$ = 1.25 x 10^{-2} M; $[Na^+]_{tot}$ = 0.1 M; 25°. The dashed-line indicates the activity of $Ni(Bipy)^{2+}$ in a buffer-free system (calculated for the above conditions with eq. 3).

constant $K = (3.5 \pm 1) \times 10^{-11}$ mol^{-1} l. sec^{-1} (I = 0.1, $NaClO_4$; 25°C),[10] must be considered rather as an upper limit. From measurements in the range of 15° to 45°C ΔE was estimated to be 15.7 Kcal mol^{-1}.

3.2. The Ni^{2+}-ethylenediamine system in the presence of borate buffer This system showed no, or only a very insignificant, background catalysis. The most active species is the Ni^{2+}-ethylenediamine 1:2 complex (*cf.* Fig. 9) which is formed to a reasonable degree only from pH 8 through 10.[23] The slope of the curve in Figure 10 increases from −1 to zero, *i.e.* with increasing pH v_0 becomes increasingly independent on $[H^+]$, obviously at pH < 8 v_0 is proportional to $1/[H^+]$. The good reproducibility of these experiments is also evidenced; the full and empty circles show results obtained by two people with a difference in time of more than two years.

The dependence of v_0 on $[H_2O_2]$ was studied at pH 8.09, 8.10, 9.22 and 9.36 under the condition $[H_2O_2]_{tot(t=0)} > [Ni(En)_2{}^{2+}]$. The plots (*cf.* Fig. 11) show that v_0 is proportional to $[H_2O_2]$. However, experiments at pH 8.10 where $[H_2O_2]_{tot(t=0)} \lesssim [Ni(En)_2{}^{2+}]$ demonstrate unequivocally that actually two molecules of H_2O_2 participate in the reaction before the rate determining step. This means, the catalyst is already present as a peroxo complex when $[H_2O_2]_{tot(t=0)} > [Ni(En)_2{}^{2+}]$. Under all conditions (Fig. 12) v_0 is proportional to $[Ni(En)_2{}^{2+}]$.

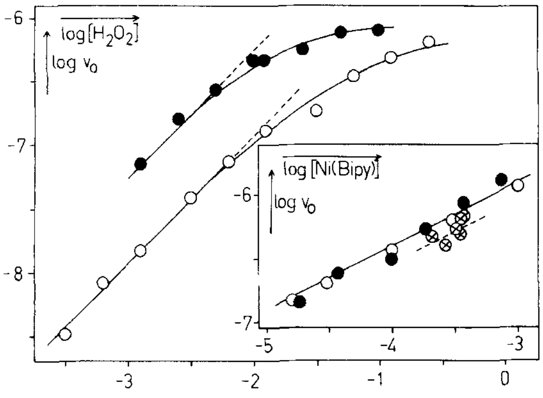


FIGURE 7 Catalase-like activity of $Ni(Bipy)^{2+}$ ($[Ni^{2+}]_{tot}$ = $[Bipy]_{tot}$ = 10^{-3} M) in dependence on $[H_2O_2]_{tot(t=0)}$ at pH 7.65 (○) and 9.60 (●); $[borate]_{tot}$ = 0.1 M; $[Na^+]_{tot}$ = 0.1 M; 25° C. – *Inserted figure:* Activity of $Ni(Bipy)^{2+}$ ($[Ni^{2+}]_{tot}$ = $[Bipy]_{tot}$ in dependence on $[Ni(Bipy)^{2+}]$ at pH 9.20 and $[H_2O_2]_{tot(t=0)} = 5 \times 10^{-2}$ M (●); $[borate]_{tot}$ = 0.1 M; $[Na^+]_{tot}$ = 0.1 M; 25° C. The results obtained from Figure 5 (⊗) are shown for the ratios $[Bipy]_{tot}/[Ni^{2+}]_{tot}$ = 0.75, 1, 1.25, 1.5, 1.75, and 2. *Calculated* v_0 (○) for the conditions of (●) with eq. 12, $k_3 = 3.82 \times 10^{-5}$ mol$^{0.5}$ l.$^{-0.5}$ sec^{-1}, and $K_M = 4.02 \times 10^{-6}$ mol l.$^{-1}$).

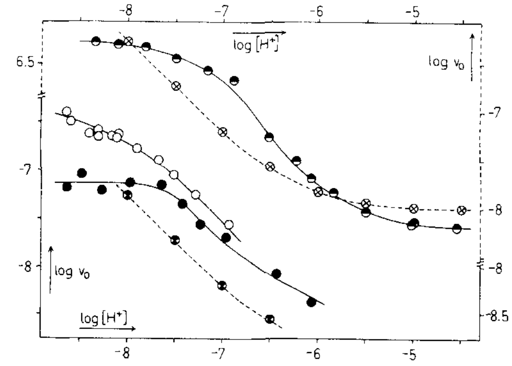


FIGURE 8 Influence of phosphate-buffer on the catalase-like activity of $Ni(Bipy)^{2+}$ ($[Ni^{2+}]_{tot}$ = [Bipy] = 10^{-3} M) at $[phosphate]_{tot}$ = 0.05 M. *Lower part:* Dependence on pH at $[H_2O_2]_{tot(t=0)} = 1.25 \times 10^{-2}$ M (●). For comparison the activity in the presence of borate (0.1 M; *cf.* Figure 6) (○) and in a buffer-free system (⊕; calculated for the above conditions with eq. 3) is also shown. *Upper part:* $[H_2O_2]_{tot(t=0)}$, = 1.25×10^{-1} M (◓). The corresponding calculated (⊗) (eq. 3) activity in a buffer-free system is given for comparison.

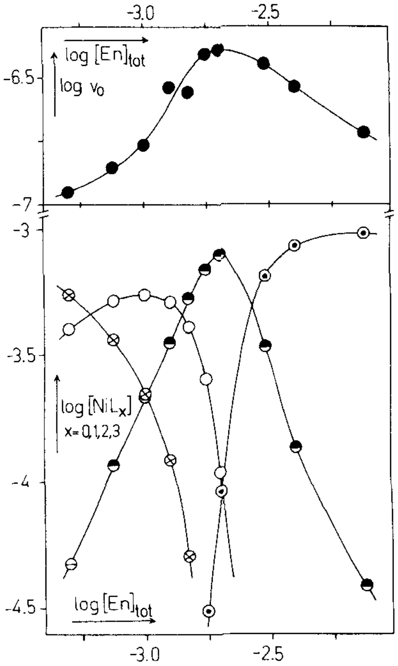


FIGURE 9 Catalase-like activity of Ni^{2+}-ethylenediamine. Dependence on $[ethylenediamine]_{tot}$ at $[Ni^{2+}]_{tot} = 10^{-3}$ M, $[H_2O_2]_{tot(t=0)} = 1.25 \times 10^{-2}$ M, and pH 9.36 ([borate] = 0.1 M). $[Na^+]_{tot}$ = 0.1 M; 25° C. The *lower part* shows the distribution of the several species[23] under the above conditions[17] in their dependence on $[ethylenediamine]_{tot}$: Ni^{2+} (⊗), $Ni(En)^{2+}$ (○), $Ni(En)_2^{2+}$ (◓), and $Ni(En)_3^{2+}$(⊙).

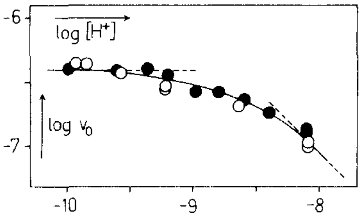


FIGURE 10 Catalase-like activity of $Ni(en)_2^{2+}$ ($[Ni^{2+}]_{tot} = \frac{1}{2}[En]_{tot} = 10^{-3}$ M) in dependence on pH. $[H_2O_2]_{tot(t=0)} = 1.25 \times 10^{-2}$ M; $[borate]_{tot} = 0.1$ M; $[Na^+]_{tot} = 0.1$ M; 25° C. $[Ni(En)_2^{2+}]$ changes over the pH range from 7.52×10^{-4} M to 7.97×10^{-4} M.[17,23]

Thus, the kinetic parameters observed in borate and in the buffer-free system are quite similar.

Nevertheless, v_0 is significantly influenced by borate (Fig. 13): At $[H_3BO_3]_{tot} < 2 \times 10^{-2}$ M v_0 is proportional to $[H_3BO_3]_{tot}$, while at concentrations $\geqslant 0.1$ M the system is saturated and the activity of $Ni(En)_2^{2+}$ is enhanced by a factor of more than 40 as compared with the borate-free system. Solutions containing all reactants but no Ni^{2+} or no Ni^{2+}-ethylenediamine showed no activity. This means, borate itself is no independent catalyst, but only an intermediate "supporter".

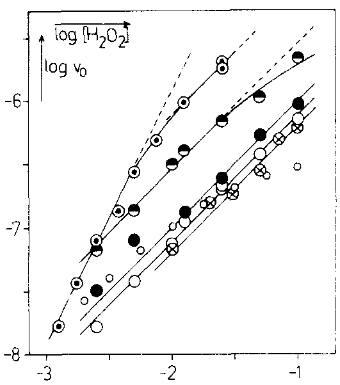


FIGURE 11 Catalase-like activity of $Ni(En)_2^{2+}$ ($[Ni^{2+}]_{tot} = \frac{1}{2}[En]_{tot}$: ●, ◓, ○, 10^{-3} M; ⊗ 2.5×10^{-4} M) in dependence on $[H_2O_2]_{tot(t=0)}$ at $[Ni^{2+}]_{tot} < [H_2O_2]_{tot(t=0)}$, and pH 8.09 (○), 8.10 (●), 9.22 (⊗), and 9.36 (◓); $[borate]_{tot} = 0.1$ M; $[Na^+]_{tot} = 0.1$ M; 25° C. Percentage of $Ni(En)_2^{2+}$ under the given conditions ($[Ni^{2+}]_{tot} = 100\%$): ○, ●, 74.8%; ⊗, 78.9%; ◓, 79.6%.[17,23] Dependence on $[H_2O_2]_{tot(t=0)}$ at $[Ni^{2+}]_{tot} \gtrsim [H_2O_2]_{tot(t=0)}$ (⊙) and pH 8.10. ($[Ni^{2+}]_{tot} = \frac{1}{2}[En]_{tot} = 10^{-2}$ M; $[Ni(En)_2] = 7.95 \times 10^{-3}$ M, $[Ni^{2+}] = 2.67 \times 10^{-5}$ M, $[Ni(En)] = 1.14 \times 10^{-3}$ M $[Ni(En)_3] = 8.75 \times 10^{-4}$ M);[17,23] $[borate]_{tot} = 0.1$ M; $[Na^+]_{tot} = 0.1$ M; 25°C. *Calculated* v_0 (○) with eq. 18 for the conditions at pH 8.09 (○).

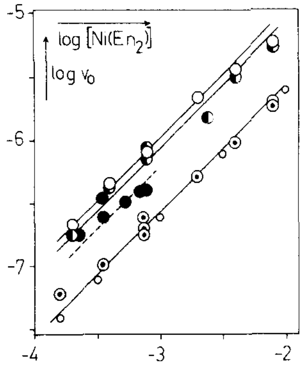


FIGURE 12 Catalase-like activity of $Ni(En)_2^{2+}$ ($[Ni^{2+}]_{tot} = \frac{1}{2}[En]_{tot}$) at pH 8.09 (⊙), 9.36 (◐) and 9.94 (○) in dependence on $[Ni(En)_2^{2+}]$. $[H_2O_2]_{tot(t=0)} = 2.5 \times 10^{-2}$ M; $[borate]_{tot} = 0.1$ M; $[Na^+]_{tot} = 0.1$ M; 25° C. The results obtained from Figure 9 (●) are shown for the ratios $[En]_{tot}/[Ni^{2+}]_{tot} = 1, 1.25, 1.5, 1.75, 2$, and 3.[17,23] – *Calculated* v_0 (○) with eq. 18 for the conditions of ⊙.

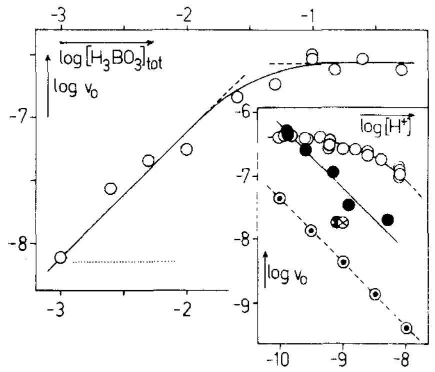


FIGURE 13 Catalase-like activity of $Ni(En)_2^{2+}$ ($[Ni^{2+}]_{tot} = \frac{1}{2}[En]_{tot} = 10^{-3}$ M; $[Ni(En)_2] = 7.95 \times 10^{-4}$ M)[17,23] at pH 9.22 and $[H_2O_2]_{tot(t=0)} = 1.25 \times 10^{-2}$ M in dependence on $[borate]_{tot}$. $[Na^+]_{tot} = 0.1$ M; 25°. The dotted line indicates the *upper* limit of the corresponding activity of $Ni(En)_2^{2+}$ in a buffer-free system; calculated with eq. 4 of Section 3.1. – *Inserted figure:* Influence of buffer-anions on the activity of $Ni(En)_2^{2+}$ ($[Ni^{2+}]_{tot} = \frac{1}{2}[En]_{tot} = 10^{-3}$ M; *cf.* legend of Fig. 10) in dependence on pH at $[H_2O_2]_{tot(t=0)} = 1.25 \times 10^{-2}$ M and $[borate]_{tot} = 0.1$ M (○, *cf.* Fig. 10), $[acetate]_{tot} = 0.1$ M (●), or $[phosphate]_{tot} = 0.1$ M (⊗; the same system but *without* Ni^{2+} gives ⊗). $[Na^+]_{tot} = 0.1$ M (in the case of phosphate $[Na^+]$ is somewhat higher); 25° C. The *upper* limit of the corresponding activity of $Ni(En)_2^{2+}$ in a buffer-free system (⊙) was calculated with eq. 4 of Section 3.1.

The activation energy was determined at pH 8.32 ($[Ni(En)_2{}^{2+}] = 7.71 \times 10^{-4}$ M) and 9.85 (7.97×10^{-4} M) in the temperature range of 5° through 45°C ($[Ni^{2+}]_{tot} = \frac{1}{2}[En]_{tot} = 10^{-3}$ M; $[H_2O_2]_{tot(t=0)} = 1.25 \times 10^{-2}$ M): $\Delta E = 16.8$ Kcal mol^{-1}[24]

3.3. The Ni^{2+}-ethylenediamine system in the presence of acetate or phosphate buffer Borate exhibits two distinct qualities: (i) It activates the catalyst, $Ni(En)_2{}^{2+}$. (ii) The impurity (*cf.* Section 3.1.) is not activated, but its activity is rather inhibited. Therefore, other buffers were also tested. With phosphate and similarly with carbonate the background catalysis is very high (*cf.* the insertion of Fig. 13), while with acetate an activation by a factor of more than 14 is observed. Here, as in the buffer-free system (*cf.* Section 3.1), v_0 is proportional to $1/[H^+]$.

4. The Ni^{2+} Systems with 2-Picolylamine, 4-Aminomethylimidazole, or Histamine as Catalysts

In Figure 14 the catalase-like activity of the Ni^{2+}-2-picolylamine system is shown at constant $[H_2O_2]_{tot(t=0)}$, pH and $[Ni^{2+}]_{tot}$ in its dependence on [2-picolylamine].[25] There is no complex species with a marked activity: it appears that Ni^{2+} and $Ni(2\text{-picolylamine})^{2+}$ have about the same effect on the rate of disproportionation of H_2O_2. Also in the Ni^{2+}-4-aminomethylimidazole and -histamine systems (*cf.* Fig. 15)[25] none of the complex species reaches even the catalytic power of Ni^{2+}.

DISCUSSION

Ni^{2+}_{aq} *as a Catalyst*

Based on the results of eq. 2 the following reaction

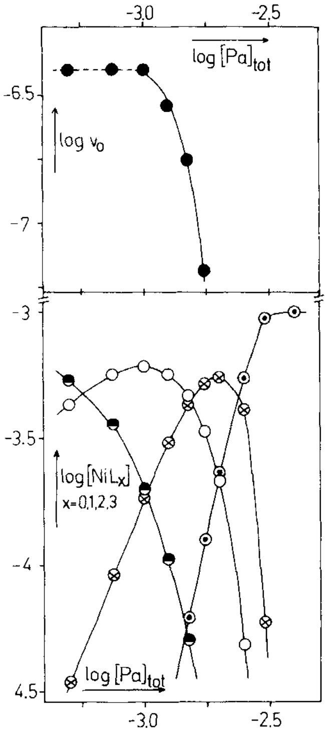


FIGURE 14 Catalase-like activity of the Ni^{2+}-2-picolylamine (2-aminomethylpyridine) system in dependence on $[\text{2-picolylamine}]_{tot}$ at $[Ni^{2+}]_{tot} = 10^{-3}$ M, $[H_2O_2]_{tot(t=0)} = 1.25 \times 10^{-2}$ M, and pH 9.36 ($[\text{borate}]_{tot} = 0.1$ M). $[Na^+]_{tot} = 0.1$ M; 25°C. The dashed line indicates uncertainty due to precipitation. The *lower part* shows the distribution of the several species[25] under the above conditions[17] in their dependence on $[\text{2-picolylamine}]_{tot}$: Ni^{2+} (◓), $Ni(Pa)^{2+}$ (○), $Ni(Pa)_2{}^{2+}$ (⊗), and $Ni(Pa)_3{}^{2+}$ (⊙).

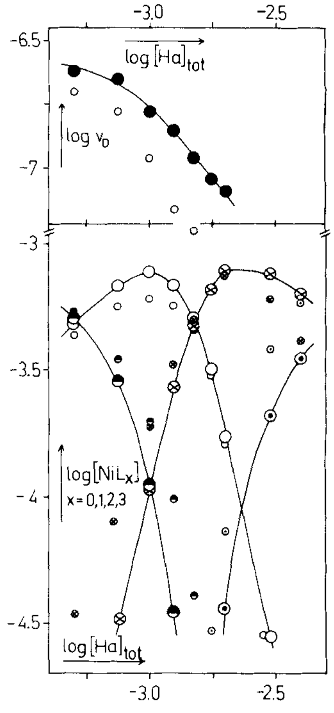


FIGURE 15 Catalase-like activity of the Ni^{2+}-histamine system in dependence on $[\text{histamine}]_{tot}$ at $[Ni^{2+}]_{tot} = 10^{-3}$ M, $[H_2O_2]_{tot(t=0)} = 1.25 \times 10^{-2}$ M, and pH 9.36 ($[\text{borate}]_{tot} = 0.1$ M). $[Na^+]_{tot} = 0.1$ M; 25°C. The *lower part* shows the distribution of the several species[25] under the above conditions[17] in their dependence on $[\text{histamine}]_{tot}$: Ni^{2+} (◓), $Ni(Ha)^{2+}$ (○), $Ni(Ha)_2{}^{2+}$ (⊗), and $Ni(Ha)_3{}^{2+}$ (⊙). — The small points refer to the Ni^{2+}-4-aminomethylimidazole system (conditions correspond to the Ni^{2+}-histamine system).[17,25]

scheme may be postulated:[26,27]

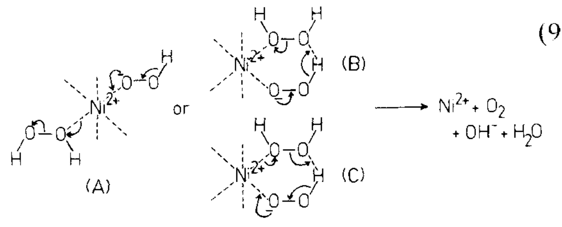
$$H_2O_2 \xrightleftharpoons{K^H_{H_2O_2}} H^+ + HOO^- \quad (5)$$

$$Ni^{2+} + HOO^- \xrightleftharpoons[k_2]{k_1} Ni(OOH)^+ \quad (6)$$

$$Ni(OOH)^+ + H_2O_2 \xrightleftharpoons[k_4]{k_3} Ni(OOH)(H_2O_2)^+ \quad (7)$$

$$Ni(OOH)(H_2O_2)^+ \xrightarrow{k_5} Ni^{2+} + O_2 + H_2O + OH^- \quad (8)$$

From eqs. 5–8 the observed rate law (eq. 2) may easily be derived, where $k = k_5 K_{H_2O_2} (k_1/k_2)(k_3/k_4)$. The rate-determining step is assumed to occur within $Ni(OOH)(H_2O_2)^+$; eq. 9 shows possible structures.



(9)

For a *trans* arrangement of the two peroxo ligands evidence was given earlier[1,5] with Co^{III}-hematoporphyrin as a catalyst, *i.e.* the electron transfer occurs through the central metal ion (*cf.* also[28,29]). A *cis* arrangement has been suggested with $Cu(2,2'\text{-bipyridyl})^{2+}$,[4,30] where two mechanisms for the electron transfer appear plausible: (i) the metal ion acts only as a clamp (*cf.* Structure B), and (ii) the electron transfer occurs through the metal ion (*cf.* C). We favor the second possibility for two reasons:[7,28] (i) If Structure B would reflect the mechanism, it would be difficult to rationalize why only redox active metal ions show a catalase-like activity. (ii) In Structure C a better use is made of the electron attracting qualities of the metal ion.

$Ni(2,2'\text{-Bipyridyl})^{2+}$ as a Catalyst

Here, the most outstanding feature is that ν_0 is proportional to $[Ni(Bipy)^{2+}]^{0.5}$ (Sections 2.1. and 2.2.) in the whole pH range from 4.3 to 10. An exponent of 0.5 may be explained by a monomer-dimer equilibrium, *e.g.* eq. 10:

$$2[(Bipy)Ni(OH)]^+ \xrightleftharpoons{K_D} [(Bipy)Ni(OH)]_2^{2+} \quad (10)$$

In case this equilibrium is on its *right* side and the monomer species is the catalytically active one, an exponent of 0.5 for the dependence between ν_0 and $[Ni(Bipy)^{2+}]$ results. However, potentiometric titrations revealed that $Ni(Bipy)^{2+}$ hydrolyzes only at pH > 8. Similar results were obtained from titrations in the presence of H_2O_2. Hence, the formation of a dimer with a large value of K_D that includes either OH^- or HOO^- must be excluded.

A dimer independent of pH could be formed with H_2O_2, but this postulation must also be rejected: (i) Though H_2O_2, has even better solvation properties than H_2O,[31] it appears unrealistic to assume that eq. 11 is completely shifted to its right side. (ii) With

$$2Ni(Bipy)^{2+} + H_2O_2 \rightleftharpoons [(Bipy)Ni(H_2O_2)Ni(Bipy)]^{4+} \quad (11)$$

$[Ni^{2+}]_{tot} > [H_2O_2]_{tot(t=0)}$ eq. 11 should become dependent upon $[H_2O_2]$, but the results give no hint for a deviation from linear proportionality between ν_0 and $[H_2O_2]$.

To conclude, we see at present no convincing hypothesis to explain the observed proportionality: $\nu_0 \sim [Ni(Bipy)^{2+}]^{0.5}$. However, it must be emphasized that the results demonstrate unequivocally that different catalytic pathways are verified by Ni^{2+}_{aq} and $Ni(Bipy)^{2+}$.

By calculating log v_0 in its dependence on pH (Fig. 3) it has been shown that the simple rate law 3 is able to account for all experimental facts of the buffer-free system (*cf.* Section 2.1.). However, in borate buffer (Section 2.2.; Fig. 6) saturation is observed, *i.e.* ν_0 is becoming independent of $[H^+]$ at higher pH values. This is taken into account in the rate law 12,[3]

$$\nu_0 = \frac{d[O_2]}{dt} = \frac{k_3[H_2O_2][Ni(Bipy)^{2+}]^{0.5}_{tot}}{(K_M/K^H_{H_2O_2})[H^+] + [H_2O_2]} \quad (12)$$

which is based on the steady-state approximation.[32] By the procedure of Eadie and Hofstee,[33] one obtains from plots of $\nu_0/[H_2O_2]$ *versus* ν_0, based on the experiments of Figure 7 at pH 7.65 and 9.60, and $[Ni(Bipy)]_{tot} = 3.71 \times 10^{-4}$ M,[34] at pH 7.65 $k_3 = 3.82 \times 10^{-5}$ mol$^{0.5}$ l.$^{-0.5}$ sec^{-1} and $K_M = 4.02 \times 10^{-6}$ mol l.$^{-1}$, and at pH 9.60 $k_3 = 4.70 \times 10^{-5}$ mol$^{0.5}$ l.$^{-0.5}$ sec^{-1} and $K_M = 7.23 \times 10^{-5}$ mol l.$^{-1}$.

The values of k_3 agree reasonably well at both pH's, while those due to K_M differ by a factor of about 18. This may be explained by a competitive inhibition, which has no influence on k_3, but changes

K_M by a factor of $(1 + K_I[I])$.[33] The concentrations of OH^- and $B(OH)_4^-$ increase with increasing pH, both species may act as inhibitors. Therefore, we consider the results obtained at pH 7.65 as the more appropriate ones (*cf.* also[18]). Using these data and eq. 12, ν_0 was calculated (empty points) in its dependence on pH for the experimental conditions of Figure 6; both series agree reasonably well. The same is true for dependence between ν_0 and $[Ni(Bipy)^{2+}]$ (*cf.* the insertion in Fig. 7).

Ni(Ethylenediamine)$_2$$^{2+}$ as a Catalyst

The rate law for $Ni(En)_2{}^{2+}$ as a catalyst in buffer-free solutions (*cf.* eq. 4) is of exactly the same form as the one obtained for Ni^{2+}_{aq} as catalyst (*cf.* eq. 2). Hence, the reaction scheme outlined in eqs. 5 to 8 can also be postulated for the catalase-like activity of $Ni(En)_2{}^{2+}$.

For $Ni(En)_2{}^{2+}$ as a catalyst in borate buffer it appears that the same proportionalities hold between v_0 and the concentration of the reactants; however, with the exception of $[H^+]$, as the following reasoning reveals. The studies under the conditions $[Ni(En)_2{}^{2+}]_{tot} \gtrsim [H_2O_2]_{tot(t=0)}$ (*cf.* Fig. 11) show, (i) that $\nu_0 \sim [H_2O_2]^2$, and (ii) that at pH 8.10 and $[Ni(En)_2{}^{2+}]_{tot}:[H_2O_2]_{tot(t=0)} = 1:2$ the 1:1 peroxo complex with $Ni(En)_2{}^{2+}$ is completely formed. Hence, as with the ratio $[Ni(En)_2{}^{2+}]_{tot}$: $[H_2O_2]_{tot(t=0)} > 1:15$ in the pH range 8 to 9 a dependence on the pH is still observed (*cf.* Fig. 10), this must mean that the first, as well as the second coordinating peroxo species is HOO^- and *not* H_2O_2. Hence, a reaction scheme similar to eqs. 5 to 8 can be outlined:[26]

$$2H_2O_2 \xrightleftharpoons{(K^H_{H_2O_2})^2} 2H^+ + 2HOO^- \tag{13}$$

$$Ni(En)_2{}^{2+} + HOO^- \xrightleftharpoons[k_2]{k_1} Ni(En)_2(OOH)^+ \tag{14}$$

$$Ni(En)_2(OOH)^+ + HOO^- \xrightleftharpoons[k_4]{k_3} Ni(En)_2(OOH)_2 \tag{15}$$

$$Ni(En)_2(OOH)_2 \xrightarrow{k_5} Ni(En)_2{}^{2+} + O_2 + 2OH^- \tag{16}$$

Based on eqs. 13 to 16 and taking into consideration that at the end of the cycle of a catalytic reaction the catalyst is restored, the rate law 17 can be derived.[35] However, eq. 17 holds only for the experimental condition $[H_2O_2]_{tot(t=0)} >$ $[Ni(En)_2{}^{2+}]_{tot}$, because the approximation $[H_2O_2]_{tot} = [H_2O_2]$ was made.

$$\nu_0 = \frac{d[O_2]}{dt} \tag{17}$$

$$= \frac{k_5[Ni(En)_2]_{tot}[H_2O_2]^2}{\frac{k_2}{k_1}\frac{k_4+k_5}{k_3}\frac{[H^+]^2}{(K^H_{H_2O_2})^2} + \left(\frac{k_5}{k_1} + \frac{k_4+k_5}{k_3}\right)\frac{[H^+]}{K^H_{H_2O_2}}[H_2O_2] + [H_2O_2]^2}$$

As the left handed curve of Figure 11 reveals (when $[H_2O_2]_{tot(t=0)} = 2\,[Ni(En)_2{}^{2+}]_{tot}$ and pH ≥ 8), eq. 14 is already shifted towards its right side, and then ν_0 is proportional only to $[Ni(En)_2{}^{2+}]_{tot}$, $[H_2O_2]_{tot(t=0)}$, and $[H^+]$ (*cf.* Fig. 10, 11, and 12). Hence, in eq. 17 the terms containing k_2/k_1 or $1/k_1$ become negligible and one obtains the simpler rate law 18 (*cf.* eq. 12 in ref.[3]):

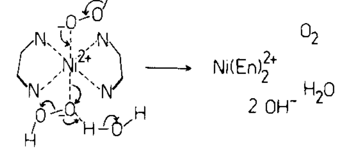
$$\nu_0 = \frac{d[O_2]}{dt} = \frac{k_5[Ni(En)_2{}^{2+}]_{tot}[H_2O_2]}{\frac{k_4+k_5}{k_3}\frac{[H^+]}{K^H_{H_2O_2}} + [H_2O_2]} \tag{18}$$

As the studies under excess $[H_2O_2]_{tot)(t=0)}$ did not lead to a significant saturation of the catalyst (*cf.* Fig. 11), we estimated $(k_4 + k_5)/k_3$ and k_5 from the data in Figure 10. With $\nu_0 = 10^{-7}$ mol $l.^{-1}$ sec^{-1} at pH 8 and $\nu_0 = 4 \times 10^{-7}$ mol $l.^{-1}$ sec^{-1} at pH 10, the conditions of Figure 10, $K^H_{H_2O_2} = 1.55 \times 10^{-12}$,[36] and eq. 18 one obtains $(k_4 + k_5)/k_3 = 5 \times 10^{-6}$ mol $l.^{-1}$ and $k_5 = 5 \times 10^{-4}$ sec^{-1}.

With these results and eq. 18 one may calculate the dependence between ν_0 and the concentration of the reactants. The calculated and measured data for the dependence between ν_0 and $[Ni(En)_2{}^{2+}]$ agree excellent (Fig. 12), while the one between ν_0 and $[H_2O_2]$ (Fig. 11) is less satisfying. This is probably because the value estimated for $(k_4 + k_5)/k_3$ is somewhat too large due to a competitive inhibition[37] by the OH^- or $B(OH)_4^-$ at higher pH values.

The stability constants of the $Ni(En)_2{}^{2+}$-peroxo adducts of eqs. 14 and 15 are given by k_1/k_2 and k_3/k_4. Based on Figure 11 (pH 8.09) one may estimate a lower limit for the stability of the 1:1 peroxo adduct: $\log K^{Ni(En)_2}_{Ni(En)_2(OOH)} \geqslant 6.4$.[38] For the stability of the 1:2 peroxo adduct (eq. 15) also a rough guess may be made as the relationship holds: $K^{Ni(En)_2(OOH)}_{Ni(En)_2(OOH)_2} = k_3/k_4 \geqslant k_3/(k_4 + k_5) = 2 \times 10^5$ hence, $\log K^{Ni(En)_2(OOH)}_{Ni(En)_2(OOH)_2} \geqslant 5.3$.[39] These values may be compared with the stability constant of the 1:1 complex between HOO^- and Co^{III}-hematoporphyrin (CoHP): $\log K^{CoHP}_{CoHP(OOH)} = 7.84$.[5] Taking into account that in both complex centers the metal ion has a formal charge of two (in CoHP one positive charge of Co^{III} is neutralized by the deprotonated ring) and that in two cases a 1:1 and in the third a 1:2 complex is formed, the orders of the three stability constants correspond well with each other. However, the decomposition of the Ni^{2+}-peroxo complex is slower by a factor of about 100, as can be seen by comparing the rate of the decomposition of $Ni(En)_2(OOH)_2$ ($k_5 = 5 \times 10^{-4}$ sec^{-1}) and $CoHP(OOH)(H_2O_2)$ ($k_5 = 6.76 \times 10^{-2}$ sec^{-1}; *cf.*[5]).

In the mechanism as given by eqs. 13 to 16 it is assumed that the rate-determining step occurs within the complex $Ni(En)_2(OOH)_2$, and thus, the question is: are the two peroxo ligands bound *cis* or *trans* to each other? As the stability constants,[23] $\log K^{Ni}_{Ni(En)} - \log K^{Ni(En)}_{Ni(En)_2} = 6.97 - 6.18 = 0.8$ and $\log K^{Ni(En)}_{Ni(En)_2} - \log K^{Ni(En)_2}_{Ni(En)_3} = 6.18 - 4.38 = 1.8$, evidence that $Ni(En)_2{}^{2+}$ prefers a *trans* orientation, the following scheme (eq. 19) may be outlined:



(D)

(19)

Obviously, Structure D in eq. 19 has one weak point: its symmetry, *i.e.* what initiates an electron transfer? In the buffer-free system v_0 is proportional only to $1/[H^+]$ (*cf.* eq. 4) and, hence, one of the HOO^- species in Structure D must be replaced by H_2O_2 which then corresponds to the asymmetric Structure A of eq. 9. In the buffer-containing system this problem could be overcome by allowing a cooperative effect of borate during the reaction. This would explain, (i) the rate enhancing effect of this buffer on the catalase-like activity of $Ni(En)_2{}^{2+}$ (*cf.* Fig. 13) and (ii) the symmetry of the two peroxo species in Structure D would be eliminated. An explanation that H_3BO_3 ($B(OH)_3$) acts as a *Lewis* acid by coordinating to HOO^- which itself is already coordinated to $Ni(En)_2{}^{2+}$ appears unsatisfactory because it is not applicable to explain the rate enhancing effect of acetate (*cf.* Fig. 13). We think that the more convincing explanation, which is applicable to borate and acetate, is the formation of peroxo intermediates, like $(H_2BO_3 \cdot H_2O_2)^-$, $(H_2BO_3 \cdot 2\,H_2O_2)^-$ (*cf.*[40]), $(HOO)B(OH)_3^-$, $(HOO)_2B(OH)_2^-$ (*cf.*[41]) and $B_2(O_2)_2(OH)_4{}^{2-}$ (*cf.*[42,43]) or $CH_3CO(O_2)^-$.[44] Hence, one HOO^- in Structure D could be replaced by such a peroxo intermediate, for which better coordinating qualities may be surmised than for HOO^- and H_2O_2. This could also favor the reactivity. Additionally, it is known that the decomposition of perborates[43] and peracetate[45] is catalyzed by a number of transition metal ions. Finally, it must be noted here that borate enhances also the catalase-like activity of Co^{2+}[46] and the oxidation of thiocyanate by H_2O_2.[41] Thus, it appears that cooperative effects of the described kind are a general feature.[47]

GENERAL CONSIDERATIONS AND CONCLUSIONS

From the present studies one may conclude that buffers influence the rate of the disproportionation of H_2O_2 but not the principal mechanism. In the case of a competitive inhibition this is easily rationalized because the buffer species may coordinate to the metal ion and thus prevent the substrate from coordination. However, where the buffer leads to an enhancement of the activity the retention of the mechanism could not be expected. As the presence of a buffer leads rather to a variation of the substrate (*cf.* the preceding section) the mechanism must be predetermined by qualities of the complex. This is in agreement with the evidence that the actual decomposition of H_2O_2 occurs within the coordination sphere of the metal ion as already indicated for Ni^{2+}_{aq} and $Ni(En)_2{}^{2+}$ in eqs. 9 and 19. The existence of 2,2′-bipyridyl-Ni^{2+}-peroxo complexes was proved spectrophotometrically.[7,48]

From a comparison of the catalytic qualities of Ni^{2+} and its complexes (Table 1) it is immediately obvious that the ligand bound to Ni^{2+} has an influence on the reaction mechanism. However, the same ligand bonded to different metal ions does not necessarily lead to the same mechanism: with $Ni(Bipy)^{2+}$ and $Cu(Bipy)^{2+}$ different reaction paths are used. On the other hand, such different complexes as $Cu(Bipy)^{2+}$ and $Co^{III}HP$ show the same kinetic parameters for their catalase-like activity.

It should also be noted, that the influence of ethylenediamine and 2,2′-bipyridyl on Ni^{2+} is able to achieve different reaction paths for the disproportionation of H_2O_2. The difference between these two amines is that one offers "aliphatic" and the other "aromatic" binding sites, the latter being able to form in addition to the σ bonds π (back donating) bonds. If Ni^{2+} is "confronted" with a mixed quality, as in the complexes of 2-picolylamine (Fig. 14), 4-aminomethylimidazole and histamine (Fig. 15) (*cf.* Section

TABLE I
Kinetic parameters of several catalase-like systems

	Proportionalities between the initial rate, v_0, and the concentration of the reactants			
	$[\text{Catalyst}]^x$	$[H_2O_2]^y$	$[H^+]^z$	
Catalyst	x	y	z	Ref.
Ni^{2+}_{aq}	1	2	–1	Section 1
$Ni(En)_2{}^{2+}$	1	2	–1; –2[a]	Section 3
$Ni(Bipy)^{2+}$	0.5	1	0; –1[b]	Section 2
$Cu(Bipy)^{2+}$	1	2	–1	4,30
$Co^{III}HP$[c]	1	2	–1	5

[a] For the buffer-free system the evidence obtained is $z = -1$ (*cf.* Section 3.1.). For the borate containing system was deduced, $z = -2$ (*cf.* the discussion part for this system).

[b] In the buffer-free system a pH-dependent as well as a pH-independent reaction was observed (*cf.* Section 2.1.); the same is true for the system with phosphate (*cf.* Section 2.3.), while in borate only the pH-dependent part was observed.

[c] Co^{III} hematoporphyrin.

TABLE II
Comparison of the initial rate of the O_2 evolution, $\nu_0 = d[O_2]/dt$ (mol l^{-1} sec^{-1}), for several catalase-like systems ($I = 0.1$; 25° C)[a]

	Normalized rates at			
Catalyst	pH 6	pH 8	pH 10	Ref.
Ni^{2+}_{aq}	0.01	1	–	b
$Ni(En)_2{}^{2+}$ [c]	–	~0.02	~2	b
$Ni(En)_2{}^{2+}$ in 0.1 M $[\text{Borate}]_{tot}$	–	6.7	27	b
$Ni(Bipy)^{2+}$	0.07	2.5	–	b
$Ni(Bipy)^{2+}$ in 0.1 M $[\text{Borate}]_{tot}$	–	19	66	b
$Cu(Bipy)^{2+}$	~1700[d]	–	–	30
$Co^{III}HP$[e]	1700	3170	3190	5

[a] The data given correspond to the conditions $[\text{catalyst}] = 10^{-3}$ M, $[H_2O_2]_{tot(t=0)} = 10^{-2}$ M and are calculated from the known rate laws for those pH values for which the validity of the rate laws was proved. All data are normalized for the catalase-like activity of Ni^{2+}_{aq} at pH 8: $\nu_0 = 1.77 \times 10^{-8}$ mol l^{-1} sec^{-1}.

[b] This work.

[c] *Cf.* Section 3.1. and footnote 20.

[d] Valid for natural ionic strength, $I < 0.004$, and under the condition that $\nu_0 = d[O_2]/dt = ½d[H_2O_2]/dt$.

[e] Co^{III}-hematoporphyrin.

4), neither the reaction path for $Ni(Bipy)^{2+}$ nor the one for $Ni(En)_2{}^{2+}$ can be verified, and "free" Ni^{2+} is the most active species.

Finally, the Ni^{2+} systems must be classified as rather poor catalysts, compared to Cu(2,2′-bipyridyl)$^{2+}$ and Co^{III}-hematoporphyrin (*cf.* Table II); this is probably because Ni^{2+} is not very redox active.[7] In the buffer-free systems at pH 8 $Ni(En)_2{}^{2+}$ is less active than free Ni^{2+}_{aq}, while in borate (*cf.* Fig. 9) this is reverse. Thus, with the mentioned exception, the Ni^{2+}-amine systems are more active than Ni^{2+}_{aq}. The rate enhancing effect of borate is obvious with $Ni(En)_2{}^{2+}$ and $Ni(Bipy)^{2+}$ as catalysts.

ACKNOWLEDGEMENTS

This investigation was supported by a research grant from Schweizerischen Nationalfonds zur Förderung der wissenschaftlichen Forschung, and by a grant from the CIBA–Stiftung (Basel). A fellowship to K.W. from the Dr. Gadient Engi–Stiftung (CIBA–GEIGY AG, Basel) during the course of his dissertation is gratefully acknowledged. The computer, IBM 1620, was made available by the Rechenzentrum der Universität Basel.

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12. The experiments with 0.1 M phosphate buffer showed a strange anomaly: in the pH range 6 to 7.5 the reaction is slow and "normal" only in the first two minutes; then nearly "explosive" liberation of O_2 occurs. Even at pH 4.8 after 20 minutes (with very small activity) a sudden evolution of O_2 is measured.
13. Calculated with the constants determined by G. Anderegg, *Helv. Chim. Acta*, **46**, 2397 (1963): $pK^{H}_{H(Bipy)} = 4.49$; $\log K^{Ni}_{Ni(Bipy)} = 7.13$, $\log K^{Ni(Bipy)}_{Ni(Bipy)_2} = 6.88$; $\log K^{Ni(Bipy)_2}_{Ni(Bipy)_3} = 6.53$.
14. At $v_0 < 10^{-8}$ the exactness is low, as the O_2 evolution is slow.
15. Calculations for the activity of Ni^{2+}_{aq}, based on Section 1.1, lead to an order comparable to the observed one. As already slight errors in the stability constants[13] effect markedly these calculations, the experimental results were not "corrected" for the activity of Ni^{2+}_{aq}. But Ni^{2+}_{aq} cannot be the most active species in this system.[16]
16. Ni^{2+} can be eliminated because the dependencies between v_0 and [reactants] are different from those in Section 1. $Ni(Bipy)_3{}^{2+}$ is eliminated due to its saturated coordination sphere.
17. Calculated without considering the presence of borate.
18. In several of the experiments in the pH range > 8.8 a precipitate was observed, which however, occurred irregularly.
19. The good reproduceability of the experiments, ◐ and ●, done by two people with a difference in time of 18 months, is obvious.
20. As Ni^{2+}_{aq} (*cf.* Section 1.1.) is more active than the Ni^{2+}-ethylenediamine 1:2 system one could argue that in the latter case the portion of uncomplexed metal ion is responsible for the observed low activity. However, we feel that the activity is due to $Ni(En)_2{}^{2+}$ because: (i) In the pH range 8.2 to 10, Ni^{2+} not bound to En will be hydrolyzed and therefore will not be available as a catalyst. (ii) For Ni^{2+}_{aq} and the Ni^{2+}-ethylenediamine system $\Delta E = 11.4$ and 15.7 Kcal mol^{-1}, respectively, *i.e.*, E_A is different and thus indicating different active species. (iii) In borate buffer $Ni(En)_2$ is unequivocally the most active species (*cf.* Fig. 9).
21. Ethylenediamine (*puriss.* p.a.) from Fluka AG was destilled twice. Preparation of the dihydrochloride and several recristallisations did also not improve the situation. The pH was adjusted with the purest commercially available NaOH (*reinst zur Analyse*) or $HClO_4$ (*suprapur*), both Merck AG. – For the Cu^{2+}-ethylenediamine system a peroxidase-like reaction (oxidation to glycine) is known.[22] The same test (thinlayer chromatography) with the ethylenediamine system in the absence or presence of Ni^{2+} was negative.
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23. Calculated with the constants: $pK^{H}_{H_2(En)} = 7.10$, $pK^{H}_{H(En)} = 9.89$, $\log K^{Ni}_{Ni(En)} = 6.97$, $\log K^{Ni(En)}_{Ni(En)_2} = 6.18$, $\log K^{Ni(En)_2}_{Ni(En)_3} = 4.38$; R. Griesser and H. Sigel, *Inorg. Chem.*, **10**, 2229 (1971).
24. The slopes of the best straight lines for $\log v_0$ *versus* 1/T (in °K) at pH 8.32 and 9.85 are -3.36×10^3 and -3.96×10^3, respectively. Average slope: $m = -3.66 \times 10^3$. $\Delta E = -m(R/0.434) = 16.8$ Kcal mol^{-1}.
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26. On the basis of kinetics studies it is not possible to distinguish between the coordination of H_2O_2 and subsequent deprotonation or direct coordination of HOO^-.
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32. $K_M = (k_2 + k_3)/k_1$. Recently,[3] the rate constant k_1 was due to the formation of $Fe^{III}PTS \cdot OOH$, k_2 due to the reverse process, and k_3 was the constant of the rate determining step of the catalysis (PTS = 4,4′,4″,4‴-tetrasulfophthalocyanine). Presently, the meaning of these constants is not defined, as no structure for the catalytically active complex could be deduced. – For

$[H^+] \gg (K^{H}_{H_2O_2}/K_M)[H_2O_2]$ eq. 12 can be reduced to the pH-dependent term of eq. 3.

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37. A competitive inhibition changes $(k_4 + k_5)/k_3$ by $(1 + K_I[I])$.[33]
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47. This does not mean that borate always leads to an acceleration of the reaction rate; sometimes borate has no effect,[3,5] or even inhibits the reaction.[41]
48. The results of ref.[7] evidence only that the complex contains one HOO^- but it is not clear if the absorbing complex is a monomer or a dimer, because $[Ni(Bipy)^{2+}]$ could not be varied for reasons of absorption and solubility.