Monatshefte für Chemie 126: 393–399 (1995)

Monatshefte für Chemie
Chemical Monthly

Printed in Austria

Kinetics and Mechanism of the Decomposition of Hydrogen Peroxide Catalyzed by Mn(II)-*bis*-Salicylaldimine Complexes

I. A. Salem, M. Y. El-Sheikh, and **A. B. Zaki**

Department of Chemistry, Faculty of Science, Tanta University, Tanta, Egypt

Summary. The tetradentate *Schiff* bases N,N′-*bis*(salicylidene) ethylenediamine (*salen*), N,N-*bis*-(salicylidene) hexylenediamine (*salhex*), and N,N′-*bis*(salicylidene)-*o*-phenylenediamine (*sal-o-phen*) are very strongly adsorbed by cation exchange resins (Dowex-50W) with manganese(II) as a counter ion, forming stable complexes. The kinetics of the catalytic decomposition of H_2O_2 in presence of these complexes has been studied in aqueous medium. The decomposition reaction is first order with respect to H_2O_2 in the case of *salen* and *sal-o-phen* and third order in the case of *salhex*. The greater the ligand methylene chain length or the greater the steric effect of the ligand, the greater will be the rate of reaction. The reaction is governed by the entropy of activation. A reaction mechanism is proposed.

Keywords. Hydrogen peroxide; Manganese; Tetradentate *Schiff* base; Kinetics; Decomposition.

Kinetik und Mechanismus der von Mn(II)-*bis*-Salicylaldimin – Komplexen katalysierten Zersetzung von Wasserstoffperoxid

Zusammenfassung. Die teradentaten *Schiff*schen Basen N,N′-*bis*-Salicyliden-ethylendiamin (*salen*), N,N′-*bis*-Salicyliden-Hexylendiamin (*salhex*) und N,N′-*bis*-Salicyliden-*o*-phenylendiamin (*sal-o-phen*) werden von Kationenaustauschen (Dowex-50W) mit Mangan(II) als Gegenion unter der Bildung stabiler Komplexe adsorbiert. Die Kinetik der katalytischen Zersetzung von H_2O_2 in Gegenwart dieser Komplexe wurde in wäßrigem Medium untersucht. Die Zersetzungsreaktion ist erster Ordnung bezüglich H_2O_2 in den Fällen *salen* und *sal-o-phen* und dritter Ordnung im Fall von *salhex*. Die Reaktionsgeschwindigkeit steigt mit der Länge der Methylenkette des Liganden und mit dessen Raumbedarf und wird von der Aktivierungsentropie bestimmt. Ein Reaktionsmechanismus wird vorgeschlagen.

Introduction

It is well established that manganese – *Schiff* base complexes play an essential role in some biological systems, *e.g.* the oxidation of water to oxygen during photosynthesis [1, 2]. Many manganese complexes have been investigated for structural and functional similarities to these systems [3, 4]. The essential step in an efficient catalyst must be the reduction of hydrogen peroxide without the formation of OH radicals which attack organic materials at near diffusion controlled rates

[5]. In general, mononuclear manganous complexes are oxidized slowly by hydrogen peroxide owing to the high reduction potentials of the manganic species [6] and the free energy of formation of the OH radical.

In our previous work we have synthesized some transition metal complexes supported on Dowex resin and silica-alumina [7–9]. Also, the heterogeneous catalytic activity of these complexes with respect to hydrogen peroxide decomposition have been studied. However, only few contributions have been made using manganese(II) complexes [8, 9]. In this work, we have extended our investigation to *bis*-salicylaldimine tetradentate *Schiff* base ligands complexed with manganese(II) bound to Dowex-50W resin. These ligands are N,N′-*bis*(salicylidene)ethylenediamine (*salen*). N,N′-*bis*(salicylidene)hexylenediamine (*salhex*), and N,N′-*bis*(salicylidene)-*o*-phenylenediamine (*sal-o-phen*). The use of solid catalysts has the advantage that the reactions can be quenched easily and that the separation of reaction intermediates is simple.

Results and Discussion

The total capacity and the moisture content of the resin were determined before and after the decomposition reaction and were found to be unchanged. Thus, the resin was not degraded during hydrogen peroxide decomposition, which demonstrates its stability under the present working conditions.

With an initial concentration of H_2O_2 equal to 2.413×10^{-2} *M*, the reaction was first order with respect to H_2O_2 in the case of *salen* and *sal-o-phen* (Fig. 1) and third order in the case of *salhex*. The rate of the decomposition reaction was increased either by extending the length of the methylene chain in the ligand (from *salen* to *salhex*) or by substituting a methylene groups by a phenyl ring (from *salen* to *sal-o-phen*, Table 1).

The k values (per g of dry resin) were used in an *Arrhenius* plot to yield the activation energy $E^{\#}$. Higher $E^{\#}$ values are found with higher rates of reaction (Table 1). This means that the reaction rate is governed by the entropy of activation [7, 12] when going either from *salen* to *salhex* or from *salen* to *sal-o-phen*.

The change in the enthalpy of activation, $\Delta H^{\#}$, the change in the free energy of activation, $\Delta G^{\#}$, and the change in the entropy of activation, $\Delta S^{\#}$, were calculated [7, 8] (Tables 1, 2). The values of $\Delta G^{\#}$ are in good agreement with those found for H_2O_2 decomposition in the presence of Dowex-50W resin in the form of manganese amine [9] and Fe(III) *Schiff* base complexes [13]. The entropy of activation increases either from *salen* to *salhex* or from *salen* to *sal-o-phen* (Table 1), indicating a rising probability of activated complex formation [13].

With the manganese(II) - *salen* complex, the weight of the resin was kept constant, whereas the initial concentration of hydrogen peroxide was varied. The order of the reaction decreased from 1.2 to 0.5 with increasing hydrogen peroxide concentration from 1.2×10^{-2} to 9.6×10^{-2} *M*; this is indicative of a stepwise mechanism [13, 14].

The reaction velocity at time zero, v_0, was determined (Table 2) [13]. The relationship between v_0 and the initial concentration of H_2O_2 at various temperatures (Fig. 2) obeys an equation of the type $v_0 = k_0 \cdot [H_2O_2]$, where k_0 is the initial rate constant (Table 2). The initial reaction order is one, in agreement with that of the

Table 1. Rate constant k (per g dry resin) and activation parameters for the decomposition of H_2O_2 ($2.4 \times 10^{-2}\,M$) in the presence of 0.4–1.0 g range air-dried resin Dowex-50W (2% *DVB*, 200–400 mesh) in the form of Mn(II) *Schiff* base complexes

Schiff base complex	n	T(°C)	$k \times 10^{-3}$ ($M^{1-n}\,s^{-1}$)	E (kJ·mol^{-1})	$\Delta G^{\#}$ (kJ·mol^{-1})	$\Delta H^{\#}$ (kJ·mol^{-1})	$\Delta S^{\#}$ (J·deg^{-1} mol^{-1})
[Mn(*salen*)]	1	25	0.0196	57.60	101.0	55.09	−150.3
		30	0.0287				
		35	0.0418				
		40	0.0596				
[Mn(*sal-o-phen*)]	1	25	0.0405	66.90	98.90	64.40	−113.0
		30	0.0647				
		35	0.0978				
		40	0.1483				
[Mn(*salhex*)]	3	25	51.600	98.69	79.96	96.15	−53.0
		30	101.60				
		35	185.10				
		40	351.60				

Table 2. Kinetic and activation parameters at time zero for the decomposition of H_2O_2 in the presence of 0.6 g air-dried resin Dowex-50W (2% *DVB*, 200–400 mesh) in the form of [Mn(*salen*)] complex ions

T(°C)	[H_2O_2] (M)	$v_0 \times 10^7$ ($M\,s^{-1}$)	$k_0 \times 10^5$ (s^{-1})	$E^{\#}$ (kJ·mol^{-1})	$\Delta G^{\#}$ (kJ·mol^{-1})	$\Delta H^{\#}$ (kJ·mol^{-1})	$\Delta S^{\#}$ (J·deg^{-1} mol^{-1})
25	0.012	1.25	2.89	48.4	100.2	45.94	−177.6
	0.024	2.80					
	0.048	6.50					
	0.096	13.8					
30	0.021	2.04	3.96				
	0.024	4.05					
	0.048	9.00					
	0.094	18.8					
35	0.012	2.96	5.32				
	0.024	5.55					
	0.048	12.5					
	0.096	24.8					
40	0.012	4.30	7.42				
	0.024	7.90					
	0.048	16.5					
	0.096	35.0					

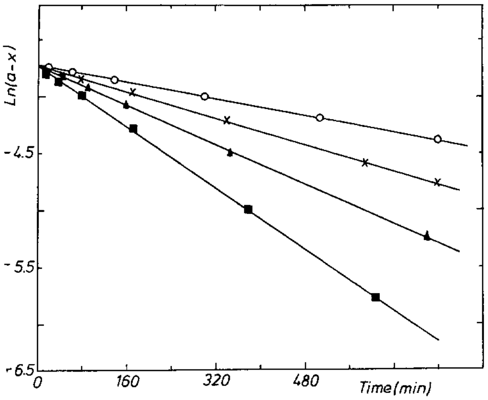

Fig. 1. First order rate equation for H_2O_2 (0.0241 *M*) decomposition in the presence of 0.4 g of air-dried resin Dowex-50W (2% *DVB*, 200–400 mesh) in the form of [Mn(*sal-o-phen*)] at different temperatures; 0: 25 °C, x: 30 °C ▲: 35°, and ■: 40 °C

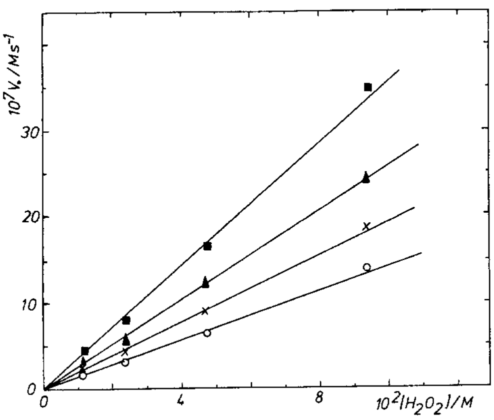

Fig. 2. Variation of the initial reaction rate v_0 with initial concentration of H_2O_2 for decomposition of H_2O_2 in the presence of 0.6 g air-dried resin Dowex-50W (2% *DVB*, 200–400 mesh) in the form of [Mn(*salen*)] at different temperatures; o: 25 °C, x: 30 °C, ▲: 35 °C, and ■: 40 °C

actual reaction in all its complexity. The equality of the two orders means that the chemical process is unaffected by secondary reactions [13, 15]. The values of the initial rate constant, k_0, (Table 2) were used in an *Arrhenius* plot and yield an activation energy of 48.4 kJ/mol. This value is smaller than the one given in Table 1 for the overall reaction under the same working conditions. This means that the degree of disorder of the Mn(II)-*salen* complex ions was greater at the beginning of the reaction with H_2O_2 than that in the case of the former (in the active species) with H_2O_2 molecules in the bulk of the reaction [13]. Also, the k_0 values were greater than the k values which supports the above explanation.

During the early stages of the reaction, the Mn(II) *Schiff* base complex reacts with hydrogen peroxide to form the active species (intermediate) and this then reacts with another H_2O_2 molecule to yield the peroxo Mn(II) complex. To verify such intermediate formation, it is necessary to carry out two reactions using the same resin (Fig. 3). The first reaction was carried out in presence of resin in association with the Mn(II) *Schiff* base complex. After completion of this reaction, the resin was collected, washed, and used in the second reaction in association with the peroxo Mn(II) complex now present on the solid matrix. The reaction rate with the peroxo complex was always greater than that with the Mn(II) *Schiff* base complex, thus providing evidence for an intermediate (active species) formed at the start of the reaction. In contrast to the effect on the rate, the reaction order with the peroxo

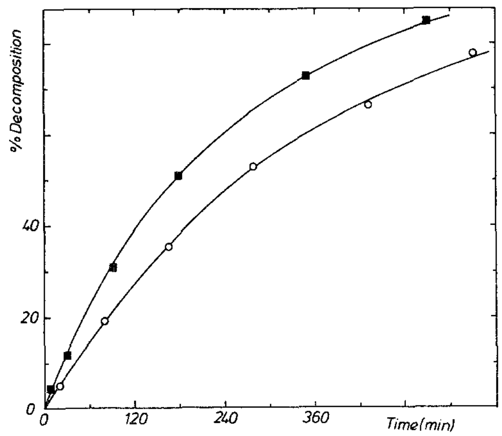

Fig. 3. Decomposition *vs.* time curves for H_2O_2 (0.0241 M) in the presence of 1.0 g air-dried resin Dowex-50W (2% *DVB*, 200–400 mesh) in the form of ○: [Mn(*salen*)] and ■: peroxo manganese complex at 40 °C

complex was equal to that observed with the Mn(II) *Schiff* base complex, demonstrating that the peroxo complex is capable of oxidizing H_2O_2.

Since the $E^{\#}$ values (Table 1) are in the range expected for a chemical reaction, the most likely mechanism is reaction through the catalyst particles [16]. The rate law for both *salen* and *sal-o-phen* systems can be written as follows [17]:

$$H_2O_2 \overset{K_1}{\rightleftharpoons} HO_2^- + H^+ \tag{1}$$

$$[MnL] + HO_2^- \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} [MnL(HO_2)]^- \tag{2}$$

$$[MnL(HO_2)]^- + HO_2^- \underset{k_{-3}}{\overset{k_3}{\rightleftharpoons}} \text{products} \tag{3}$$

Assuming steady state conditions for $[Mn(HO_2)]^-$, where K_1 is the rapidly established equilibrium and k_{-3} is negligibly small, the rate law of the first-order dependence can be written as follows:

$$\text{Rate} = -\frac{d[H_2O_2]}{dt} = k_2 \cdot K_1 \cdot [MnL] \cdot [H_2O_2]/[H^+] \tag{4}$$

For the manganese(II)-*salhex* system, essentially the same mechanism applies except that now a third HO_2^- particle has to interact before decomposition to products occurs.

$$H_2O_2 \overset{K_1}{\rightleftharpoons} HO_2^- + H^+ \tag{1'}$$

$$[Mn(salhex)] + HO_2^- \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} [Mn(salhex)(HO_2)]^- \tag{2'}$$

$$[Mn(salhex)(HO_2)]^- + HO_2^- \underset{k_{-3}}{\overset{k_3}{\rightleftharpoons}} [Mn(salhex)(HO_2)_2]^{2-} \tag{5}$$

$$[Mn(salhex)(HO_2)_2]^{2-} + HO_2^- \xrightarrow{k_4} \text{products} \tag{6}$$

Similar treatment by the steady state hypothesis for $[\mathrm{Mn}(\mathit{salhex})(\mathrm{HO_2})]^-$ and $[\mathrm{Mn}(\mathit{salhex})(\mathrm{HO_2})_2]^{2-}$ leads to a more complicated rate law exhibiting a third order dependence on $[\mathrm{H_2O_2}]$:

$$\mathrm{Rate} = -\frac{d[\mathrm{H_2O_2}]}{dt} = \frac{k_2 \cdot k_3 \cdot k_4 \cdot K_1 \cdot [\mathrm{Mn}(\mathit{salhex})] \cdot [\mathrm{H_2O_2}]^3}{(k_{-2} \cdot [\mathrm{H^+}]^2 + k_3 \cdot K_1 \cdot [\mathrm{H^+}] \cdot [\mathrm{H_2O_2}]) \cdot (k_{-3} \cdot [\mathrm{H^+}] + k_4 \cdot K_1 \cdot [\mathrm{H_2O_2}])} \qquad 7$$

The peroxo manganese complex with *salen* and *sal-o-phen* (equation 3) may have the formula $[\mathrm{Mn}L(\mathrm{HO_2})_2\mathrm{O_2}]^{2-}$, which decomposes spontaneously to $[\mathrm{Mn}L]$, $2\mathrm{OH}^-$, and $\mathrm{O_2}$ [8].

In case of *salhex*, the peroxo complex (equation 6) may have the formula $[\mathrm{Mn}L(\mathrm{HO})_3(\mathrm{O_2})_{1.5}]^{3-}$, which decomposes spontaneously to $[\mathrm{Mn}L]$, $3\mathrm{OH}^-$ and $1.5\mathrm{O_2}$.

Experimental

The *Schiff* base ligands *salen*, *salhex*, and *sal-o-phen* were prepared according to standard procedures [10, 11] and characterized by their melting points, IR and NMR spectra, and by elemental analysis. Dowex-50W resin (2% divinyl benzene (*DVB*), 200–400 mesh) was used. The resin has been described previously [8, 9]. Its moisture content (20.5%) was determined by drying samples overnight at 110 °C at normal pressure. The total capacity of the exchanger was determined by the batch method and was equal to 5.16 meq/g $\mathrm{H^+}$. The resin was converted into the Mn(II) form by equilibrating it with $\mathrm{Mn(ClO_4)_2}$ in ethanol (0.001 *M*) using the batch process. Thereafter, the resin was collected and washed with ethanol until free from any excess of Mn(II) ions. A precalculated amount of ethanolic solution of the *Schiff* bases (0.001 *M*) was then added to the resin in the Mn(II) form to form the 1:1 complex. A small excess amount of the ligand was added in order to confirm the formation of a 1:1 complex, and the mixture was stirred for *ca.* 1 h under an atmosphere of dry argon. The resin was collected and washed with ethanol until the residual ligand was undetectable by UV spectroscopy. The colour of the resin was faint-brown with all three ligands.

A 30% hydrogen peroxide solution (a.r. grade, Merk-Schuchardt, Munich, Germany) was used. Four different concentrations of $\mathrm{H_2O_2}$ were chosen in the 1.2–9.6×10^{-2} *M* range by dilution with doubly-distilled $\mathrm{H_2O}$. The initial concentration of $\mathrm{H_2O_2}$ was determined iodometrically.

Kinetic measurements

A number of flasks (100 ml) containing a weighed quantity of the resin in the $[\mathrm{Mn}L(\mathrm{H_2O})]$ form together with doubly distilled $\mathrm{H_2O}$ (19 ml) were placed in a water shaker thermostat for 30 min. Standard $\mathrm{H_2O_2}$ stock solution (1 ml) was added quickly *via* a micropipette, and zero time was taken at the half addition point.

After a measured time, the reaction was quenched by quickly filtering the mixture through sintered glass (G2). Aliquots of the aqueous phase (5 ml) were withdrawn with a micropipette and the undecomposed $\mathrm{H_2O_2}$ was determined iodometrically. The reaction temperature was varied between 25 and 40 °C ± 0.1 °C.

Before the addition of $\mathrm{H_2O_2}$, the *pH* of the doubly distilled $\mathrm{H_2O}$ in presence of the resin had an average value of 6.85. After the addition of $\mathrm{H_2O_2}$, the *pH* increased gradually and had an average value of 7.4 at the end of the reaction.

Attempts to carry out the decomposition reaction in the presence of an acid or buffer solution led to regeneration of the resin and decomposition of the manganese(II) – *Schiff* base complexes. The rate constant *k* per g dry resin was obtained graphically using an integration method described previously [7,8].

References

[1] Pecoraro V. L. (1986) Photochem. Photobiol. **48**: 249
[2] Ashmawy F. M., McAuliffe C. A., Parish R. V., Tames J. (1984) J. Chem. Soc. Chem. Commun. 14
[3] Mobad B., Tachuagues J. P., Hawang Y. T., Hendricksen N. D. (1985) J. Am. Chem. Soc. **107**: 2802
[4] Bodini M. E., Sawyer D. T. (1976) J. Am. Chem. Soc. **98**: 8366
[5] Rush J. D., Moskos Z. (1990) Inorg. Chem. **29**: 897
[6] Yamaduchi K. S., Sawyer D. T. (1985) Isr. J. Chem. **25**: 164
[7] Salem I. A., Salem M. A., Gemeay A. H. (1993) J. Mol. Catal. **84**: 67
[8] El-Sheikh M. Y., Habib A. M., Ashmawy F. M., Gemeay A. H., Zaki A. B. (1989) J. Mol. Cata. **55**: 396
[9] Salem I. A. (1994) Int. J. Chem. Kinetic **26**: 341
[10] Pfeiffer P., Hesse T., Pfitzinger H., Shcoll W., Thielert T. (1937) J. Prakt. Chem. **149**: 217
[11] Titus S. T. E., Barr W. M., Taylor L. T. (1979) Inorg. Chim. Acta **32**: 103
[12] Wilkins R. G. (1974) The Study of the Kinetics and Mechanism of Reactions of Transition Metal Complexes. Allyn and Bacon, Boston, p. 101
[13] El-Sheikh M. Y., Ashmaway F. M., Salem I. A., Zaki A. B., Nickel U. (1991) Transition Met. Chem. **16**: 319
[14] Espenson J. H. (1981) Chemical Kinetics and Reaction Mechanism. McGraw-Hill, New York, p. 93
[15] Pannetier G., Souchay P. (1967) Chemical Kinetics, Chapter 4. Elsevier, New York
[16] Helfferich F. (1962) Ion Exchange. McGraw-Hill, New York, p. 528
[17] El-Sheikh M. Y., Habib A. M., Gemeay A. H., Zaki A. B., Bargon J. (1992) Transition Met. Chem. **17**: 299

Received May 15, 1994. Accepted October 20, 1994