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Heterogeneous Kinetic Studies of the Hydrogen Peroxide Decomposition with Some Transition Metal-Heterocyclic Complexes

S. A. EL-SAFETY, M. Y. EL-SHEIKH, M. A. SALEM, A. B. ZAKI

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

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ABSTRACT: The heterocyclic compounds piperidine (Pip), piperazine (Pz), morpholine (Morph), and N-methyl piperazine (N-MPz) were used as ligands to form transition metal complexes with Ni(II), Cu(II), and Co(II) ions. These complexes were supported on Dowex-50W resin so as to form new potential active catalysts for H_2O_2 decomposition in an aqueous medium. In all cases the reaction showed a first-order kinetics with respect to H_2O_2 concentration, except with Co(II) complexes, the reaction showed a second-order kinetics with 2% divinyl benzene (DVB) (50–100 mesh and 200–400 mesh). The rate constant k (per gram dry resin) was evaluated with a resin of cross-linkage 2 and 8% DVB (50–100 mesh) and 2% DVB (200–400 mesh) over temperature range 25–40°C. With a given resin cross-linkage, the rate constant has the following order: Ni(II) complexes < Co(II) complexes < Cu(II) complexes. With Pz ligand, k increased in the following sequence: Ni(II) complexes < Cu(II) complexes < Co(II) complexes. The reaction mechanisms of the first- and second-order kinetics were discussed and the activation parameters were deduced. © 2001 John Wiley & Sons, Inc. *Int J Chem Kinet* 33: 617–624, 2001

INTRODUCTION

The catalytic decomposition of H_2O_2 has received considerable attention and has recently been used as a source of oxygen for enhanced bioremediation of contaminated subsurface environments [1–3]. The decomposition of H_2O_2 in alkali, e.g. NaOH, KOH, and

NH_4OH , solutions has been studied in the presence of high amounts of metal ions [4–8]. The decomposition reaction was found to be of first order [4]. The second-order reaction was shown by the addition of complexing agents which reduce the activity of the metal ion contamination [6,7].

The catalytic decomposition of H_2O_2 was studied in the presence of cation exchange resin in the form of transition metal complexes in aqueous medium [9–16]. In the initial stages, the transition metal complex reacts with a H_2O_2 molecule to form the active species and

Correspondence to: S. A. El-Safety; e-mail: saes@dec1.tanta.eun.eg.
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the latter then reacts with another molecule of H_2O_2 to yield the product [17,18]. The mechanism is the same in both homogeneous and heterogeneous reactions in presence of ion exchange resin [19]. A brown peroxo-copper complex, a green peroxo-nickel complex, and a violet peroxo-chromium complex were formed at the beginning of the homogeneous catalytic decomposition of H_2O_2 [20–23]. The colored compounds are stable, even after reactions have been completed [22,23]. Furthermore, the modified transition metal complexes silica–alumina (25% Al_2O_3) and natural metal oxide-coated sand have been used as a catalyst for H_2O_2 decomposition [24–27]. The initial concentration of H_2O_2 has a great influence on the reaction rate [24,26]. The role of the produced oxygen radical intermediates (e.g. $\dot{\text{O}}\text{H}$, HO_2/O_2) has been investigated in the surface catalyzed H_2O_2 decomposition [24,27,28].

One of the objectives of the present work has been focused on utilizing Dowex-50W resin in the form of Co(II), Cu(II), and Ni(II) complexes with some heterocyclic ligands such as piperidine (Pip), piperazine (Pz), morpholine (Morph), and *N*-methyl piperazine (N-MPz). These resin-supported complexes were used as potentially active catalysts toward the H_2O_2 decomposition in aqueous solution. The kinetic and the activation parameters of H_2O_2 decomposition have been evaluated.

EXPERIMENTAL

Materials

Ion exchange resins Dowex-50W resin (2 and 8% divinyl benzene (DVB), 50–100 mesh) and 2% DVB (200–400 mesh) in the hydrogen form have been used. The moisture content of the resin sample was determined by drying at 110°C overnight under atmospheric pressure. Values of 30.4 and 17.5% moisture content were found for 2 and 8% DVB (50–100 mesh) respectively, and 20.9% for 2% DVB (200–400 mesh). Also, the total weight capacity of the resin was determined statically by the batch method [29]. The capacity was 4.667 and 3.67 meq H^+/g dry resin for 2 and 8% DVB (50–100 mesh) respectively, and 3.91 meq H^+/g dry resin for 2% DVB (200–400 mesh). The resin sample was converted into the transition metal form by equilibrating it with metal salt solution (0.1 M), and then the resin sample was collected and washed thoroughly with doubly distilled H_2O to remove any traces of the remaining ion and then added to an ethanolic solution of the desired ligand (0.1 M). The mixture was stirred for ca. 2 h. The sample was collected and washed with ethanol followed with doubly distilled H_2O until a

negative result with phenolphthalein was obtained [30]. Thirty percent volume of H_2O_2 (from Merck) was used. H_2O_2 concentration was in the 5×10^{-3} – 15×10^{-3} M range and was standardized iodometrically.

Kinetic Measurements

A number of conical flasks (100 cm^3) containing a definite amount of the catalyst with 19-ml doubly distilled H_2O were placed in a water-shaker thermostat for 30 min. For each conical flask, standard H_2O_2 stock solution (1 ml) was added quickly with a micropipette and the time was recorded. After a set interval of time, an aliquot volume (10 ml) was transferred into another flask to quench the reaction. The undecomposed H_2O_2 was determined iodometrically [9,11,14,16].

pH Measurements

The pH measurements were carried out by means of Crison Digit-101 pH meter.

Determination of the Stoichiometry and Stability Constants of the Complexes

The stoichiometry and the stability constants of the complexes were determined in the presence of KNO_3 as an inert electrolyte by Job's method (Table I) [31].

Table I The Stability Constants of the Metal-Heterocyclic Complexes in Solution, the Degree of Conversion (x/a) After 25 min, and the Rate Constant of the Decomposition Reaction of H_2O_2 (0.01 M) With 8% DVB Resin at 25°C

Type of Complex	Stability Constant (l mol^{-1})	x/a (10^{-2})	k ($10^{-4} \text{ M}^{1-n} \text{ s}^{-1}$)
Cu(II)–NMPz	99.9	11.3	60.6
Cu(II)–Pip	46.8	7.81	40.7
Cu(II)–Morph	12.0	1.33	6.70
Cu(II)–Pz	2.10	0.457	2.30
Co(II)–Pip	33.4	4.59	23.5
Co(II)–Pz	18.7	2.90	14.8
Co(II)–NMPz	6.20	2.66	13.6
Co(II)–Morph	3.32	0.62	3.08
Ni(II)–Pip	10.5	0.28	1.40
Ni(II)–NMPz	2.80	0.18	0.89
Ni(II)–Pz	0.30	0.12	0.59
Ni(II)–Morph	0.20	0.04	0.17

RESULTS AND DISCUSSION

The pH value of the reaction medium (resin–metal–heterocyclic complexes + H_2O + H_2O_2) was found to be in the range 7.1–7.33 at the beginning of the reaction. No remarkable change has been found during the decomposition reaction [32]. This means that the H_2O_2 decomposition reaction was carried out in the neutral medium with Ni(II)-, Co(II)-, and Cu(II) heterocyclic complexes. However, it was difficult to carry out the decomposition reactions in both acidic and alkaline buffer solutions, because the complex was easily regenerated in acidic buffer solution and the H_2O_2 is self-decomposed in alkaline buffer [9–15]. Besides, the hydroxide anion of alkaline solution may decompose the complex through the exchanging ligand process on the surface of the catalyst [16].

The complexes were very stable on the resin and no bleeding of the complex occurred in solution [13,14,32]. The catalytic reaction was carried out at different H_2O_2 concentrations in 5×10^{-3} – 15×10^{-3} M range and at fixed amount of the catalyst. Typical decomposition–time curves are depicted in Fig. 1. The most obvious feature of the H_2O_2 decomposition is that an induction period was observed at low concentration of H_2O_2 (5×10^{-3} M) [33] with 8% DVB (50–100 mesh) for Cu(II)–Pip and Cu(II)–Morph complexes. On the contrary, in the case of Co(II)–Pip complex, an induction period was observed at higher concentration of H_2O_2 (1×10^{-2} – 1.5×10^{-2} M), while at concentration 5×10^{-3} M the induction period

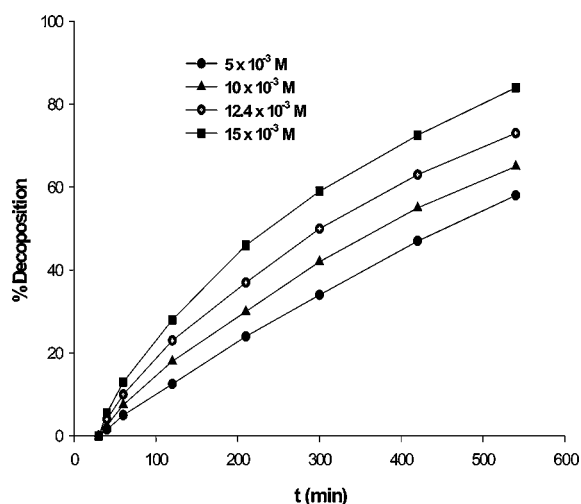


Figure 1 Illustration of the decomposition–time curve of the decomposition of H_2O_2 in the presence of 2.0 g of the air-dried resin Dowex-50W 8% DVB (50–100) mesh in the form of Ni(II)–Morph complex ions at 35°C and various concentrations of H_2O_2 .

disappeared. This can be attributed to the formation of an intermediate active species, which may have an inhibition effect on the reaction rate [34]. Our experiment exhibited that the induction period disappeared by increasing the mesh size of the Dowex-50W resin from 50–100 mesh to 200–400 mesh, as in the case of Cu(II)–Pip complex. The same behavior was observed by decreasing the degree of resin cross-linkage, as in the case of Ni(II)–Morph complex.

The Reaction Order

The first-order kinetics with respect to H_2O_2 concentration was applied for the catalytic reaction with the most metal–heterocyclic complexes with different percentages of DVB, while the Co(II)–Pip, Co(II)–Pz, and Co(II)–Morph complexes for 2% DVB (200–400 mesh) as well as the Co(II)–Pip and Co(II)–Pz complexes for 2% DVB (50–100 mesh) showed a second-order kinetics. The kinetic studies of H_2O_2 decomposition exhibited that the catalytic effectiveness of the complex is found to be a function of the degree of conversion (x/a) of H_2O_2 substrate (Table I). However, the degree of conversion of H_2O_2 (x/a) for metal–Pip complexes with 8% DVB (50–100 mesh) decreases in the following order: Ni(II)–Pip < Co(II)–Pip < Cu(II)–Pip, which represents the same sequence of the catalytic activity of these catalysts (Table I). Moreover, the degrees of conversion (x/a) at 25°C and after 25 min of the second-order reaction with 2% DVB (50–100 mesh) for Co(II)–Pip and Co(II)–Pz complexes were 1×10^{-5} and 2×10^{-5} , respectively. This result reflects that the greater the reaction order, the lower the degree of conversion and the slower the reaction rate (Tables I and II). The order of reaction at $t \rightarrow 0$ was determined and was equal to 1 with 8% DVB (50–100 mesh) for metal–heterocyclic complexes. The equality of both orders means that the chemical process is unaffected by the secondary reaction [35].

The Rate Constant of the Reaction

The rate constant k per gram dry resin, (pgdr) was calculated and summarized in Table II according to the following equation [36]:

$$\ln \frac{a}{(a-x)} = kwt \quad (1)$$

where a is the initial concentration of H_2O_2 , x is the amount of H_2O_2 decomposed at time t , and w is the amount (g) of the dry resin; this equation is depicted in Fig. 2.

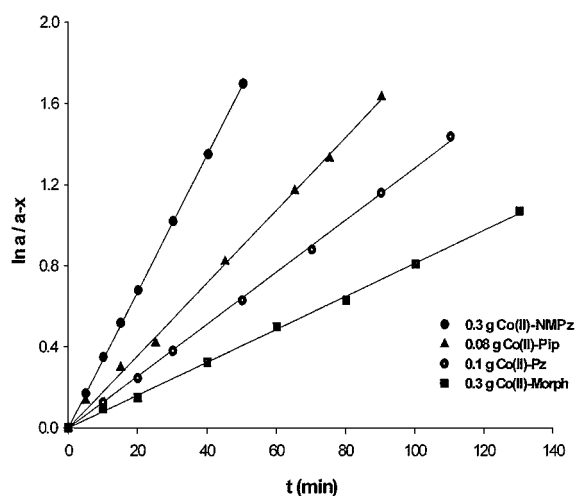
Table II The Rate Constant (k) (pgdr) and Activation Parameters for the Decomposition of H_2O_2 (0.01 M) in the Presence of 2 and 8% DVB (50–100 mesh) and 2% DVB (200–400 mesh) Resin in the Form of Co(II) –Pip Complex

%DVB	Order	t (°C)	k ($10^{-4} \text{ M}^{1-n} \text{ s}^{-1}$)	E (kJ mol^{-1})	ΔH^\ddagger (kJ mol^{-1})	ΔG^\ddagger (kJ mol^{-1})	ΔS^\ddagger ($\text{J deg}^{-1} \text{ mol}^{-1}$)
8	1	25	23.5	49.6	47.1	89.0	–137.2
		30	35.1				
		35	46.0				
		40	62.2				
2	2	25	0.6	60.8	58.3	98.2	–130.7
		30	0.9				
		35	1.3				
		40	1.9				
2*	2	25	0.8	43.1	40.5	97.3	–185.7
		30	1.1				
		35	1.6				
		40	2.0				

*2% DVB (200–400 mesh).

At a given reaction order, the rate constant (k) of H_2O_2 decomposition reaction with metal-heterocyclic complexes decreases with increasing the resin cross-linkage (Table II). This is due to salting-out effect [29,37]. The complexes of Co(II) –Pip and Co(II) –Pz with 8% DVB were more active than those with 2% DVB, suggesting the lower catalytic effectiveness of these complexes with higher reaction order (Table II). Also, the effective surface area has a greater influence on the rate constant [29]. In the case of Cu(II) complexes with 8% DVB, the rate constant k (pgdr) increased in the following sequence:

$\text{Cu(II)}\text{--Pz} < \text{Cu(II)}\text{--Morph} < \text{Cu(II)}\text{--Pip} < \text{Cu(II)}\text{--N-Mpz}$ (Table I), and in the case of Co(II) complexes the sequence was as follows: $\text{Co(II)}\text{--Morph} < \text{Co(II)}\text{--N-Mpz} < \text{Co(II)}\text{--Pz} < \text{Co(II)}\text{--Pip}$ (Table I, Fig. 2). However, in the case of Ni(II) complexes the following order was found: $\text{Ni(II)}\text{--Morph} < \text{Ni(II)}\text{--Pz} < \text{Ni(II)}\text{--N-Mpz} < \text{Ni(II)}\text{--Pip}$ (Table III). It is clear that the greater the stability constant of the complex, the higher is the rate constant of the reaction (Tables I and III) [38].

**Figure 2** Illustration of the integrated first-order equation for the decomposition of H_2O_2 ($5 \times 10^{-3} \text{ M}$) in the presence of the air-dried resin Dowex-50W 8% DVB (50–100 mesh) in the form of Co(II) –heterocyclic complexes at 35°C .

Initial Reaction Rate

The reaction rate velocity (V_0) at $t \rightarrow 0$ (Table IV), i.e. $V_0 = [dx/dt]_{t \rightarrow 0}$ was determined by extrapolation of the reaction rate–time curves to zero time (Fig. 3). The relationship between V_0 and the initial concentration of H_2O_2 obeys an equation of type $V_0 = k_0 [\text{H}_2\text{O}_2]_0$, where k_0 is the initial rate constant (Table IV) [14,16]. However, the straight line passing through the origin has been obtained with all types of transition metal-heterocyclic complexes, except in the case of Cu(II) –Pip, Co(II) –Morph, and Ni(II) –Morph, which gives an intercept with the abscissa (Fig. 4). This means that the reaction does not start unless the initial H_2O_2 concentration is greater than its value with the intercept. However, the formation of the active species required a certain redox potential, which is realized only above this H_2O_2 concentration. It would seem that the initial rate constant k_0 (pgdr) is greater than the k value for all metal-heterocyclic complexes, as shown in Tables I and IV. This means that the rate of the formation of active species was greater than the rate of the decomposition reaction of H_2O_2 [20–22].

Table III The Rate Constant (k) (pgdr) and Activation Parameters for the Decomposition of H_2O_2 (0.01 M) With 8% DVB Resin in the Form of Ni(II)-Heterocyclic Complexes

Complexes	$t(^{\circ}\text{C})$	$k (10^{-4} \text{ M}^{1-n} \text{ s}^{-1})$	$E (\text{kJ mol}^{-1})$	$\Delta H^{\#} (\text{kJ mol}^{-1})$	$\Delta G^{\#} (\text{kJ mol}^{-1})$	$\Delta S^{\#} (\text{J deg}^{-1} \text{ mol}^{-1})$
Ni(II)–Pip	25	1.39	43.4	40.9	96.3	–181.5
	30	1.94				
	35	2.56				
	40	3.24				
Ni(II)–NMPz	25	0.89	37.5	35.0	97.6	–205.0
	30	1.18				
	35	1.48				
	40	1.85				
Ni(II)–Pz	25	0.59	31.1	28.5	98.9	–230.3
	30	0.69				
	35	0.88				
	40	1.05				
Ni(II)–Morph	25	0.17	40.7	38.2	101.7	–83.7
	30	0.24				
	35	0.31				
	40	0.38				

Activation Parameters

The k and k_0 values are used in Arrhenius plots to determine the activation energy E (Tables III and IV). The E values increased with an increasing degree of resin cross-linkage in the case of Cu(II) and Co(II) complexes. The greater the percentage of DVB, the smaller the free water content, the larger the solvated complex ion (activated complex), the larger the equivalent volume of the resin, and the higher the swelling pressure. The higher the latter, the greater the tendency for the solvent and solute molecules (H_2O_2 molecules) to be squeezed out of the resin [29], and consequently

the higher the E value should be [14]. On the other hand, the value of E decreased with an increasing degree of resin cross-linkage in the case of Co(II)–Pip, Cu(II)–Pip, and Ni(II)–Pip complexes (Table II). This is due to dipole–dipole interactions of the polar solvent molecule (H_2O) with the polar group of the solute (H_2O_2) [29]. The smaller the amount of the free solvent in the resin, the less significant is the influence of the dipole–dipole interactions and then the smaller is the activation energy [11].

Generally, the more stable complexes should give higher E and lower k values as in the case of Cu(II) complexes for 2 and 8% DVB (50–100 mesh) as well

Table IV Initial Rate (V_0), Initial Rate Constant (k_0) (pgdr), and Activation Parameters for the Initial Decomposition of H_2O_2 in the Presence of 8% DVB (50–100 mesh) Resin in the Form of Piperidine–Co(II) Complex Ions

$t(^{\circ}\text{C})$	$[\text{H}_2\text{O}_2]$ (10^{-3} M)	V_0 (10^{-6} M s^{-1})	k_0 ($10^{-3} \text{ M}^{1-n} \text{ s}^{-1}$)	E (kJ mol^{-1})	$\Delta H^{\#}$ (kJ mol^{-1})	$\Delta G^{\#}$ (kJ mol^{-1})	$\Delta S^{\#}$ ($\text{J deg}^{-1} \text{ mol}^{-1}$)
25	5.0	1.00	3.06	39.5	37.0	88.6	–168.9
	10.0	2.00					
	12.5	3.00					
	15.0	3.75					
30	5.0	1.33	4.14				
	10.0	2.75					
	12.5	4.17					
	15.0	5.00					
35	5.0	1.83	5.16				
	10.0	3.50					
	12.5	5.17					
	15.0	6.33					
40	5.0	2.13	6.64				
	10.0	4.25					
	12.5	6.16					
	15.0	7.33					

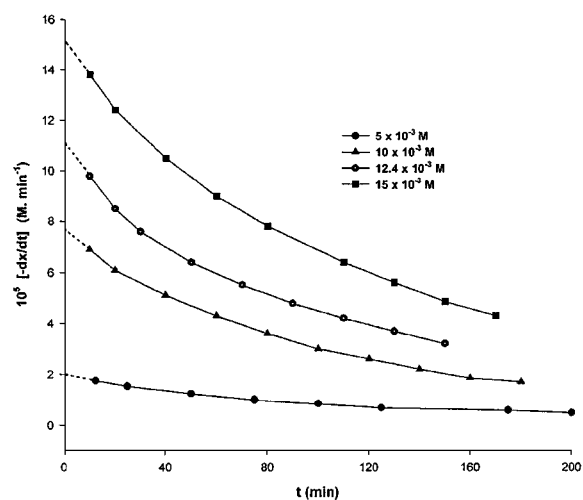


Figure 3 Illustration of the reaction-rate curves for the decomposition of H_2O_2 in the presence of 0.4 g of the air-dried resin Dowex-50W 8% DVB (50–100 mesh) in the form of Cu(II) –Pip complex ions at 25°C and various concentrations of H_2O_2 .

as in the case of Ni(II) and Co(II) complexes for 2% DVB (50–100 mesh and 200–400 mesh). Conversely, the H_2O_2 decomposition reaction with the Co(II) - and Ni(II) complexes for 2 and 8% DVB (50–100 mesh) showed the greater rate constant with higher E values, except in the case of Ni(II) –Morph complex with 8% DVB, which shows an inverse sequence (Table III). It may be attributed to the high stability of the reactant species of complex H_2O_2 molecules [39]. The E value

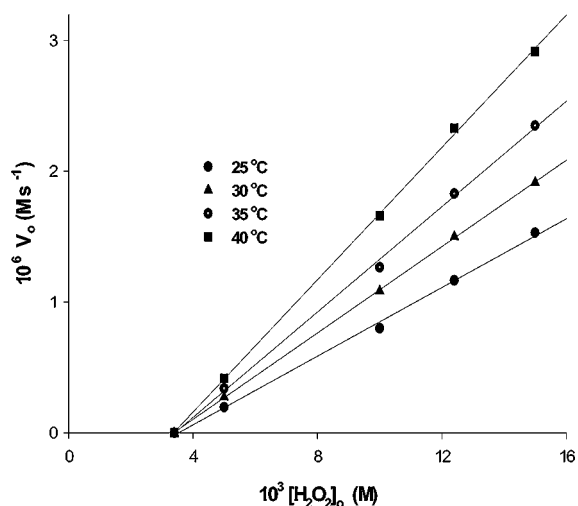


Figure 4 The relationship between the initial reaction rate and the initial concentration of H_2O_2 with constant amount (0.02 g) of the air-dried resin Dowex-50W 8% DVB (50–100 mesh) in the form of Cu(II) –Pip complex ions at different temperatures.

at $t \rightarrow 0$ (Table IV) was smaller than that corresponding to the overall reaction (Table II) with 8% DVB resin [40–42]. This means that the energy necessary for the formation of the active species (intermediate) at the beginning of the reaction was smaller than that necessary for the H_2O_2 decomposition. The ΔH^\ddagger value of activation is in the range of the chemical reaction control [29,38]. The ΔG^\ddagger value of activation was found to be in the 81–101 kJ mol^{-1} range. This value is in good agreement with that found in the literature [14,16,43]. This means that the rate of H_2O_2 decomposition reaction with metal-heterocyclic complexes is almost consistent with that found in the other studies elsewhere [44]. The greater the ΔS^\ddagger values, the greater is the probability of the activated complex formation (Tables III and IV) [45,46].

Isokinetic Relationship

The plot of ΔH^\ddagger vs. ΔS^\ddagger for the H_2O_2 decomposition with the supported Cu(II) -, Co(II) -, and Ni(II) heterocyclic complexes on 2 and 8% DVB (50–100 mesh) and 2% DVB (200–400 mesh) gives a straight line (correlation coefficient 0.98) whose slope β (isokinetic temperature) is equal to 238 K, which is smaller than the mean experimental value (305.5 K) (Fig. 5) [47]. This suggests that the catalytic reactions are entropy-controlled [48,49]. The existence of this linear relationship (Fig. 5) provides good evidence that the H_2O_2 decomposition reaction by the resin-supported metal-heterocyclic complexes follows one similar mechanism [10].

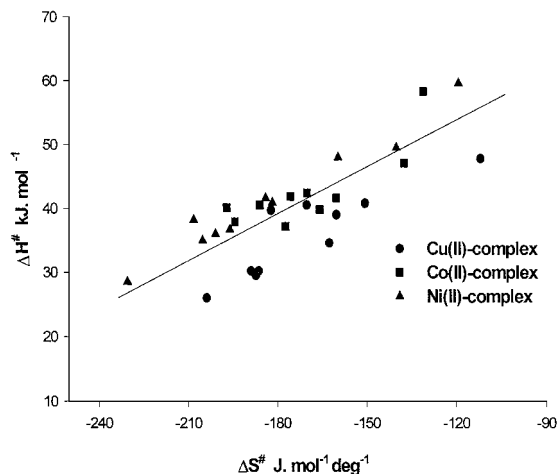
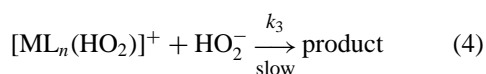
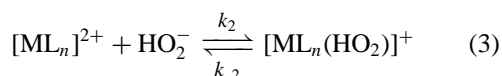
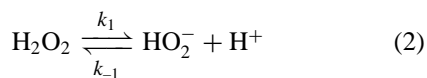


Figure 5 Isokinetic relationship of the H_2O_2 decomposition with the supported metal-heterocyclic complexes on Dowex-50W 2 and 8% DVB (50–100 mesh) and 2% DVB (200–400 mesh).

Reaction Mechanism

Since E values are in the range expected for a chemical reaction, the most likely mechanism is reaction throughout the catalyst particles [29,50].

The rate laws for the first- and second-order reaction can be derived from the following suggested mechanism:



The complex $[\text{ML}_n(\text{HO}_2)]^+$ in Eq. (3) represents the intermediate (active species), which reacts with HO_2^- in the rate-determining step (Eq. (4)).

$$dx/dt = k_3[\text{ML}_n(\text{HO}_2)]^+[\text{HO}_2^-] \quad (5)$$

Assuming steady-state approximation for the formation rate of $[\text{ML}_n(\text{HO}_2)]^+$,

$$\begin{aligned} d[\text{ML}_n(\text{HO}_2)]^+/dt &= k_2[\text{ML}_n]^{2+}[\text{HO}_2^-] \\ &- k_{-2}[\text{ML}_n(\text{HO}_2)]^+ - k_3[\text{ML}_n(\text{HO}_2)]^+[\text{HO}_2^-] = 0 \end{aligned} \quad (6)$$

$$[\text{ML}_n(\text{HO}_2)]^+ = \frac{k_2[\text{ML}_n]^{2+}[\text{HO}_2^-]}{k_{-2} + k_3[\text{HO}_2^-]} \quad (7)$$

Therefore, we can derive the generalized rate law,

$$dx/dt = \frac{k_2k_3[\text{ML}_n]^{2+}[\text{HO}_2^-]^2}{k_{-2} + k_3[\text{HO}_2^-]} \quad (8)$$

In the case of the first-order reactions, it is supposed that $k_3[\text{HO}_2^-] \gg k_{-2}$, whereas in the case of the second-order reactions, it supposed that $k_{-2} \gg k_3[\text{HO}_2^-]$ [15]. Thus, Eq. (8) can be written down for the first- and second-order reactions as follows: respectively;

$$dx/dt = k_2[\text{ML}_n]^{2+}[\text{HO}_2^-] \quad (9)$$

and

$$dx/dt = K_2k_3[\text{ML}_n]^{2+}[\text{HO}_2^-]^2 \quad (10)$$

By applying the preequilibrium equations, the rate equation for the first- and second-order can be written

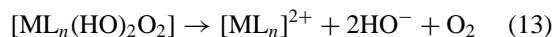
as follows:

$$\frac{dx}{dt} = \frac{K_1k_2[\text{ML}_n]^{2+}[\text{H}_2\text{O}_2]}{\text{H}^+} \quad (11)$$

and

$$\frac{dx}{dt} = \frac{K_1k_2k_3[\text{ML}_n]^{2+}[\text{H}_2\text{O}_2]^2}{k_{-2}[\text{H}^+]^2} \quad (12)$$

The source of the inverse $[\text{H}^+]$ dependence is merely due to the protolytic equilibrium (Eq. (2)). The intermediate (active species) $[\text{ML}_n(\text{HO}_2)]^+$ was also suggested in the proposed mechanism for H_2O_2 decomposition with resin-copper(II) complexes containing ethanol amines [42]. The peroxo-metal complex, which is formed as a product in Eq. (4), may have the formula $[\text{ML}_n(\text{HO})_2\text{O}_2]$, which decomposed spontaneously [14,20], as follows:



The reaction rate with peroxo-metal complex was always greater than that with the transition metal complex (Fig. 6). This experiment provides evidence for an intermediate (active species) formed at the beginning of the reaction, which had an inhibiting effect on the overall rate. The autodecomposition of peroxo-metal complex led to the evolution of oxygen and caused the original color of the complex ions to be reattained [40–42].

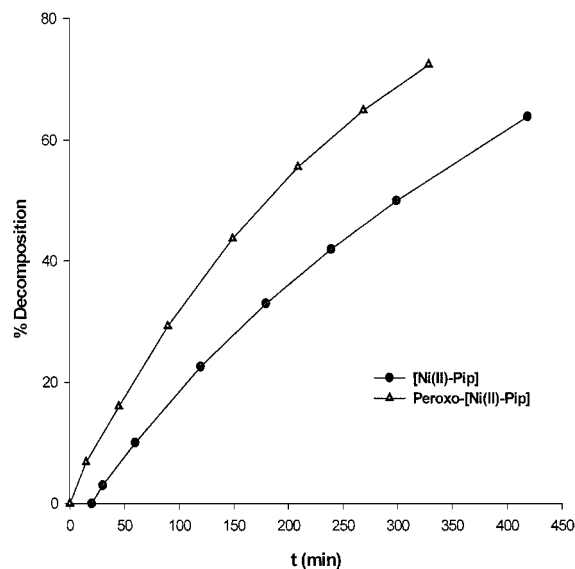


Figure 6 Illustration of the decomposition-time curves for the peroxo-reaction decomposition of H_2O_2 (0.01 M) in the presence of 0.5 g of the air-dried resin Dowex-50W 8% DVB (50–100 mesh) in the form of Ni(II)–Pip complex at 30°C.

CONCLUSION

It is noteworthy to mention that the present investigation threw light on the importance of the new potentially active resin-supported catalysts, which have biological effects and have a wide application in industry [51,52]. The current study has focused on the interaction of H_2O_2 with metal-heterocyclic complexes on Dowex-50W resin. The rate of the reaction increases with an increasing degree of conversion and with a lowering reaction order. The rate constant of reaction and the catalytic activity of the complexes are dependent on the stability constant of the complexes.

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