Kinetics of the Double Ligand Exchange between Manganese(II) Complexes and Trisoxalatocobaltate(III) in Dimethylformamide–Water Mixtures

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The kinetics of the double exchange of ligands between Mn bipy^{2+} or Mn phen^{2+} and a trisoxalatocobaltate(III) complex was studied in dimethylformamide (DMF)–water media. The reaction kinetics were followed spectrophotometrically in the temperature range of 20—40 ± 0.1 °C. The rates of the reactions were found to decrease with increasing DMF in the medium. The solvent effect on the reaction rate was discussed in terms of the dielectric constant of the medium and the thermodynamic properties of activation. A chain mechanism was proposed to account for the exchange process.

Key words kinetics; ligand exchange; solvent effect; complex

The characterization of metal–phenanthroline complexes is important for investigations concerning the storage of solar energy,[1] while the complexes of manganese(II) play an important role in enzyme reactions.[2] According to the current theoretical treatments,[3,4] changes in dielectric properties are expected to affect the reorganization of solvent molecules around the reactants and the intermediate activated complex. The solvent composition has been found to affect the reaction rates in somewhat different ways.[5,6] An interesting situation exists when two multidentate complexes are mixed and a double ligand exchange occurs.[7] The ligand substitution reaction of the monobipyridyl complex of Mn(II) has been investigated in aqueous solution.[8] In the present work, one aim to shed light on the kinetics and mechanism of the double ligand exchange reaction of Mn bipy^{2+} or Mn phen^{2+} with a trisoxalatocobaltate(III) complex. The investigations were intended to study the reaction kinetics in different dimethylformamide (DMF)–water solvent mixtures. One also aimed to study the effect of the solvent mixture and its dielectric constant on the rate of the reaction at different temperatures.

Experimental

Analar reagent quality chemicals were used throughout. Mn bipy^{2+} and Mn phen^{2+} were prepared in doubly distilled water by adding solutions of $MnCl_2 \cdot 4H_2O$ to 2,2′ bipyridyl and 1,10 phenanthroline monohydrochloride solutions, respectively. Relatively high concentrations of Mn^{2+} (*ca.* 0.86 mol l^{-1}) were used to attain a maximum degree of complexation (0.997) with phen or bipy ligands. A complex of potassium trisoxalatocobaltate(III) trihydrate was prepared as described in the literature.[9] Kinetics runs were performed in 1 cm cells of Unicam UV2-100 UV/VIS Spectrometer V3.32 at $\lambda = 600$ nm (absorption band of trisoxalatocobaltate(III) complex) where absorption changes were observed, in the temperature range of 20—40 ± 0.1 °C. All solutions were allowed to equilibrate at the desired temperature before mixing. The compositions of mixed solvents are quoted by weight before mixing. The ionic strength was kept constant using 1 M sodium perchlorate solution.

Results and Discussion

To determine the stoichiometry of the reaction, a known concentration of the trisoxalatocobaltate(III) complex (5×10^{-4} mol l^{-1}) was fixed while varying the concentrations of Mn bipy^{2+} and Mn phen^{2+}, and the absorbance of each reaction mixture was measured at various time intervals until a constancy of absorbance was observed. Applying Yoe–Jones methods,[10] an inflection was observed at the ratio 1 : 1. Therefore, the stoichiometry of the reaction can be represented by the following equation:

$$[Mn(L\text{-}L)]^{2} + [Co(oxal)_3]^{3-} = [Co(oxal)_2L\text{-}L]^{1-} + Mn\ oxal$$

where L-L represents α,α' bipyridyl (bipy) or 1,10 phenanthroline (phen), while oxal represents oxalate ligand. However, applying Mauser's method[11] the presence of only one linear independent reaction was proved.

The course of the reaction kinetics was followed by measuring the change in the absorbance at 600 nm, the λ_{max} of the trisoxalatocobaltate(III) complex, under pseudo-first order conditions with a large excess of $[Mn(L\text{-}L)]^{2+}$ complexes. To attain a maximum degree of complexation, a large excess of $MnCl_2$ solution was used. The concentrations used were: for phen and bipy 4×10^{-3} mol l^{-1}, trisoxalatocobaltate(III) 5×10^{-4} mol l^{-1}, manganese chloride 0.86 mol l^{-1}, and so the formed complex Mn phen^{2+} or Mn bipy^{2+} was then 3.988×10^{-3} mol l^{-1}. The pseudo-first order rate constants, k_{obs}, were calculated from the slopes of the linear plots of $\log(A - A_\infty)$ *vs.* time, where A represent the absorbance at time t and A_∞ is the absorbance when a complete reaction occurs. The values of the calculated k_{obs} values are collected in Table 1. A large excess of $MnCl_2$ diminished the presence of free bipy or phen ligand and it was observed that the rate constants increased with an increase in the concentration of the complex [Mn bipy]$^{2+}$ or [Mn phen]$^{2+}$ in presence of a large excess of $MnCl_2$ as shown in Fig. 1.

The solvent composition effect on the reaction kinetics was investigated in water–DMF solvent mixtures up to 90 wt% DMF, and the calculated k_{obs} value in different solvent compositions and temperatures are collected in Table 1. It was observed that the rate of both reactions decreased gradually with an increasing DMF content in the medium, *i.e.* with decreasing the dielectric constant of the solvent mixture. However, a linear dependence of $\log k$ on the reciprocal of the dielectric constant was obtained according to the Amis equation[12] at different tempera-

Table 1. Pseudo-First Order Rate Constant for the Substitution Reactions of Mn bipy^{2+} and Mn phen^{2+}

DMF (wt%)	i) For Mn bipy^{2+}				ii) For Mn phen^{2+}			
	$10^3 k_{obs}$ (s^{-1})			E (kJ mol^{-1})	$10^3 k_{obs}$ (s^{-1})			E (kJ mol^{-1})
	20	30	40 (°C)		20	30	40 (°C)	
0	0.794	1.236	1.995	34.69	0.596	1.047	1.828	43.03
10	0.735	1.189	1.905	36.01	0.507	0.933	1.737	46.55
20	0.661	1.096	1.822	38.29	0.437	0.871	1.661	51.56
30	0.588	1.035	1.738	40.91	0.372	0.759	1.585	55.68
40	0.525	0.912	1.662	43.52	0.309	0.692	1.514	60.77
50	0.457	0.832	1.585	46.99	0.251	0.589	1.413	67.02
60	0.388	0.759	1.479	54.39	0.219	0.549	1.374	70.52
70	0.298	0.606	1.232	53.08	0.182	0.432	1.023	65.36
80	0.282	0.549	1.072	50.48	0.176	0.394	0.881	60.92
90	0.251	0.478	0.955	48.71	0.167	0.355	0.741	56.57

[phen]=[bipy]=4×10^{-3} mol l^{-1}, [Mn^{2+}]=0.86 mol l^{-1}, [Co(C$_2$O$_4$)$_3^{3+}$]=5×10^{-4} mol l^{-1} and [Mn bipy^{2+}]=[Mn phen^{2+}]=3.988×10^{-3} mol l^{-1}.

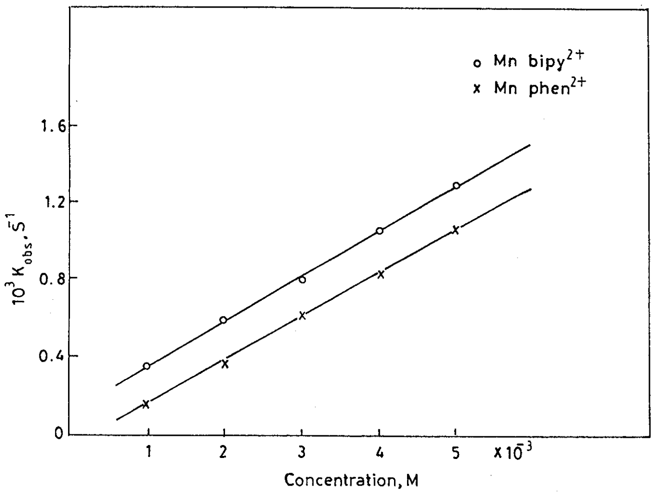

Fig. 1. Effect of Concentration on the Reaction Rate at 20 °C

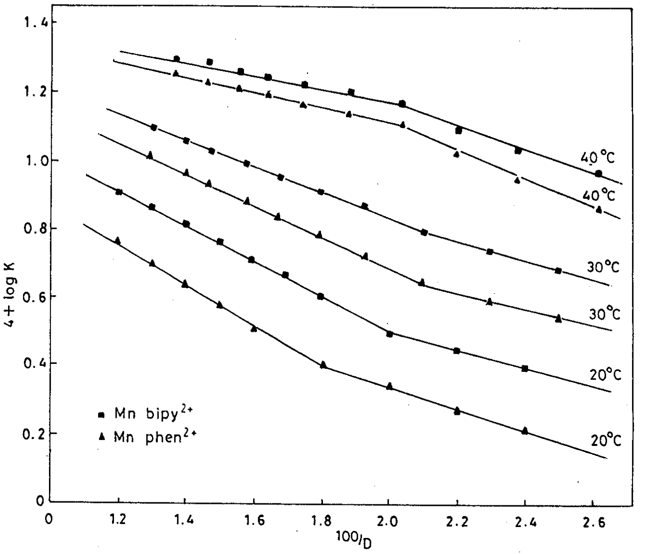

Fig. 2. Effect of Dielectric Constant on the Reaction Rates at Different Temperatures

Table 2. Observed Rate Constants at Constant Dielectric Constants, k_d, and the Isodielectric Activation Energies, E_d

Dielectric constant D	i) For Mn bipy^{2+}				ii) For Mn phen^{2+}			
	$10^3 k_d$ (s^{-1})			E_d (kJ mol^{-1})	$10^3 k_d$ (s^{-1})			E_d (kJ mol^{-1})
	20	30	40 (°C)		20	30	40 (°C)	
40	0.233	0.512	1.096	58.49	0.149	0.369	0.902	69.63
50	0.311	0.689	1.452	58.31	0.215	0.448	1.303	67.88
60	0.491	0.927	1.746	47.96	0.299	0.693	1.528	60.92
70	0.614	1.109	1.884	42.38	0.415	0.881	1.754	53.96
80	0.762	1.312	2.046	37.34	0.532	1.067	1.871	48.57

tures, as shown in Fig. 2. These linear plots indicate the formation of an activated complex more polar than the reactants. From these, the interpolated values of k_{obs} at a constant dielectric constant were obtained at different temperatures and were used to calculate the isodielectric activation energies E_d, and are given in Table 2. These values increase with an increase in DMF content, indicating solvation of the activated complex to a lesser extent than the reactants.[13]

The reactions were carried out at three temperatures in the range of 20—40±0.1 °C in various DMF–H$_2$O mixtures to construct Arrhenius plots as represented in Fig. 3, where two isokinetic temperatures were observed. In Fig. 3a, for the reaction of Mn bipy^{2+}: 52.6 °C characteristic of the rate constant 3.105×10^{-3} s^{-1} as determined in the mixtures between 0—60% DMF, and 8.5 °C corresponding to the rate constant $k_{obs}=1.288\times10^{-4}$ s^{-1} of the mixtures with DMF content higher than

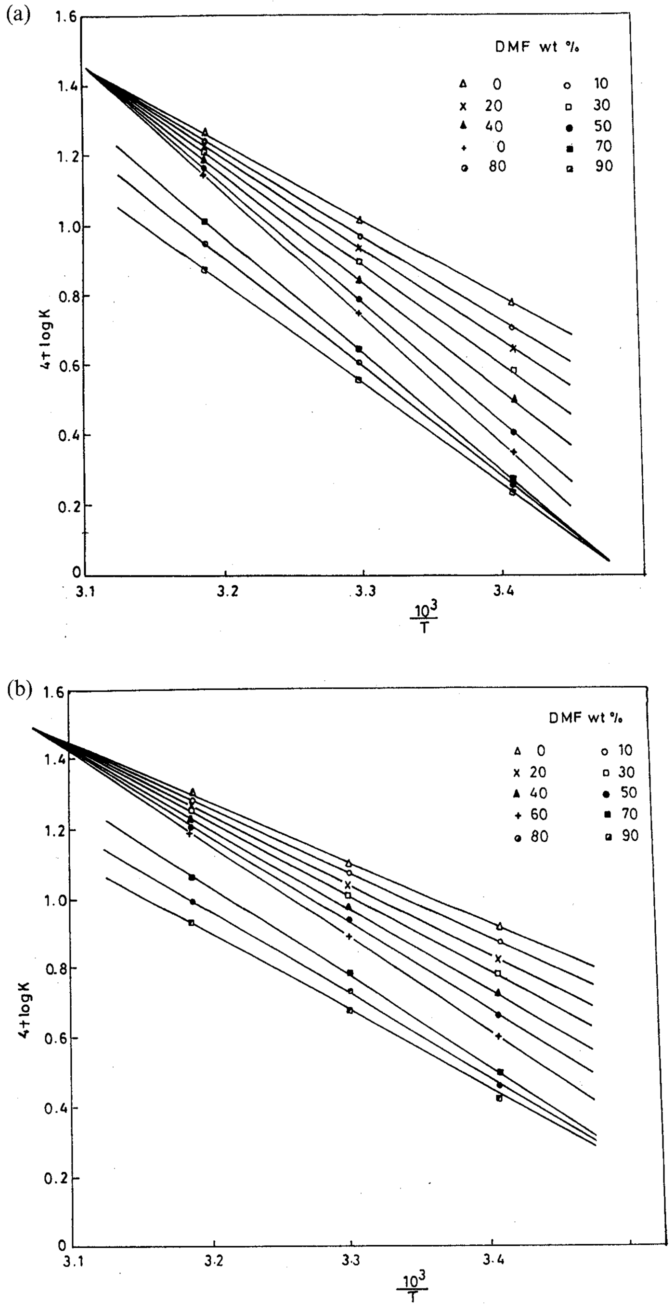

Fig. 3. Arrhenius Plots for the Substitution Reactions of Mn bipy^{2+} (a) and Mn phen^{2+} (b) in Different Solvent Compositions

60%. In Fig. 3b, for the reaction of Mn phen^{2+}, the two isokinetic temperatures are: 49.2 °C corresponding to $k_{obs} = 2.818 \times 10^{-3}\,s^{-1}$ and 14.2 °C corresponding to $k_{obs} = 1.079 \times 10^{-4}\,s^{-1}$ in the mixtures of 0—60% and higher than 60% DMF, respectively. This composition coincides with the formation of the preferential structure of associated molecules DMF $(H_2O)_3$.[14] From the slopes of Arrhenius plots, the isocomposition activation energies were calculated and are given in Table 1. It is seen that for both reactions, the value of the activation energy, increases passing through a maximum at 60% DMF, in accordance with the preferential structure of DMF with water molecules. This behavior is proof of the higher solvation of the reactants in comparison with that of the transition state, which increases the activation energy of the system in agreement with the Laidler–Eyring equation.[15] The manner in which the activation energy at a constant composition, E, and the activation energy at a constant dielectric constant, E_d, varies with solvent composition was investigated. The activation energy at a constant concentration exhibits a maximum at about 60 wt% DMF, while the activation energy at a constant dielectric constant does not. On the high dielectric constant, $E_d > E$.

Table 3. Thermodynamic Activation Parameters for the Substitution Reactions at 20 °C in Different DMF–H_2O Mixtures

DMF (wt%)	i) For Mn bipy^{2+}			ii) For Mn phen^{2+}		
	$\Delta H^{*a)}$	$\Delta G^{*a)}$	$-\Delta S^{*b)}$	$\Delta H^{*a)}$	$\Delta G^{*a)}$	$-\Delta S^{*b)}$
0	32.25	89.14	194.1	40.61	89.84	167.9
10	33.57	89.33	190.2	44.11	90.23	157.3
20	36.16	89.59	181.2	49.12	90.60	141.5
30	38.47	89.87	175.3	53.24	90.99	128.8
40	41.08	90.15	167.4	58.33	91.44	113.0
50	44.55	90.49	156.7	64.58	91.95	93.4
60	51.95	90.82	132.5	68.08	92.28	82.06
70	50.64	91.53	139.5	62.92	92.73	101.7
80	48.4	91.66	148.8	58.48	92.81	117.1
90	46.31	91.95	155.7	54.13	92.93	132.4

a) In $kJ\,mol^{-1}$. *b)* In $J\,mol^{-1}\,K^{-1}$.

The effect of solvent mixtures on the reaction rates may also be examined in terms of changes in the activation parameters. These parameters are usually taken as a measure of the solvation effect. The activation energy values were used to calculate the activation thermodynamic parameters, the enthalpy ΔH^*, the ΔS^* and the free energy ΔG^*, which are listed in Table 3. It is seen that ΔG^* increases gradually with the increase in DMF content as a sign of solvation of the reaction species.[16] The values of activation entropy and activation enthalpy increase in the series of the investigated mixtures passing through a maximum for the composition of 60% DMF for both of the two exchange reactions. The variation in thermodynamic parameters of activation at around 60 wt% DMF reflect the variation in reaction kinetics with a solvent composition.

From the above results we noticed that the reaction rates increased with an increase in concentration of the Mn L-L complex which may dissociate to give the free ligand L-L, which may catalyze the exchange reaction. The reaction rates were observed to increase also by increasing the concentration of Mn^{2+}. At the same time, the presence of one independent linear reaction based on Mauser's method was assigned. As a result, the rate can be easily controlled by the addition of traces of free ligands which greatly accelerate the exchange. Therefore, from the observed results, a chain mechanism can be proposed in which the free ligands, bipy, phen and oxal, are chain centers:

$$[Mn(L\text{-}L)]^{2+} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} Mn^{2+} + L\text{-}L \tag{1}$$

$$L\text{-}L + [Co(oxal)_3]^{3-} \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} [Co(oxal)_2L\text{-}L]^{1-} + oxal^{2-} \tag{2}$$

$$oxal^{2-} + [Mn(L\text{-}L)]^{2+} \xrightarrow{k_3} Mn\ oxal + L\text{-}L \tag{3}$$

$$\mathrm{oxal}^{2-} + \mathrm{Mn}^{2+} \xrightarrow{k_4} \mathrm{Mn\ oxal} \qquad (4)$$

Equation 1 is the chain initiation, which provides a small concentration of bipy or phen to the system. Equations 2 and 3 are chain propagating reactions which maintain the chain centers. Equation 4 and the reverse reaction of Eq. 1 are chain terminating. The rate of the reaction is determined by the two chain propagation steps (Eqs. 2, 3) resulting in the following equation:

$$\mathrm{rate} = k_2[\mathrm{L\text{-}L}][\mathrm{Co(oxal)}_3^{3-}] = k_3[\mathrm{oxal}^{2-}][\mathrm{Mn(L\text{-}L)}^{2+}] \qquad (5)$$

The formation of a mixed ligand complex $[\mathrm{Co(oxal)}_2\ \mathrm{L\text{-}L}]^{-1}$ has been prepared and characterized spectrophotometrically.17) The negative activation entropy values confirm the formation of a more dense structure by a more bulky ligand (bipy or phen), and also that the activated complex $[\mathrm{Co(oxal)}_2\mathrm{L\text{-}L}]^{1-}$ results from $[\mathrm{Co(oxal)}_3]^{3-}$ in accordance with the extended Huckel theory.

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