

Mechanism of Ligand Substitution Reaction of Monobipyridyl Complex of Manganese(II)

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The kinetics of ligand substitution reaction of Mnbipy^{2+} complex with the trisoxalatocobalt(III) has been investigated spectrophotometrically at 600 nm. The reaction follows a first order kinetics. The rate of reaction increases with increase in [bipyridyl] in the reaction mixtures. Activation parameters have been evaluated. A mechanism consistent with the results has been suggested.

Complexes of Mn(II) are important due to their role in enzyme reactions¹. The kinetics of complex formation of Mn(II) with bipyridyl was recently studied in different acidic solutions². The relatively low value of the stability constant^{3,4} of the complex, Mnbipy^{2+} (4×10^{-4}), which is in accord with the low complexation reactivity of Mn^{2+} aqua ion led us to undertake the title investigation. The results of such studies using the trisoxalatocobalt(III) are reported in this note.

The substitution reaction was studied in the temperature range of 20-40°C, since in this temperature range the rate constant for the thermal decomposition of $\text{K}_3[\text{Co}(\text{C}_2\text{O}_4)_3]$ is extremely low².

Mnbipy^{2+} complex was prepared in doubly distilled water using Merck grade $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$ and 2,2'-bipyridyl. The complex $\text{K}_3[\text{Co}(\text{C}_2\text{O}_4)_3] \cdot 3\text{H}_2\text{O}$ was prepared according to the method described before⁵. The reaction was followed at 600 nm, the λ_{max} of trisoxalatocobalt(III) using a Unicam SP 1800 UV spectrophotometer. All solutions were allowed to equilibrate at the desired temperature for 1 hr before mixing.

In a series of runs the [trisoxalate complex] was kept constant at $5 \times 10^{-4} \text{ mol dm}^{-3}$ while varying $[\text{Mnbipy}^{2+}]$. Under these conditions, the reaction followed first order kinetics as revealed by the linear plot of $2 + \log (A_t - A_\infty)$ versus time. It is seen that the rate constant decreased with increase in the concentration of MnCl_2 and bipyridyl mixtures (Table 1). To attain maximum degree of complexation ($\alpha = 0.997$) large excess of MnCl_2 solution was used (0.86 mol dm^{-3}).

Table 1—Rate Constants at Different Concentrations of MnCl_2 and Bipy

[[$\text{K}_3[\text{Co}(\text{C}_2\text{O}_4)_3]$] = $5 \times 10^{-4} \text{ mol dm}^{-3}$ at 28°C]]				
$[\text{MnCl}_2]_0$ (mol dm^{-3})	$[\text{bipy}]$ (mol dm^{-3})	Degree of complexation	$10^4[\text{Mnbipy}^{2+}]$ (mol dm^{-3})	$10^3 k_1$ (s^{-1})
5×10^{-4}	5×10^{-4}	0.15	0.73	9.3
1×10^{-3}	1×10^{-3}	0.25	2.34	3.6
2×10^{-3}	2×10^{-3}	0.35	6.88	2.4

The kinetic measurements were performed at three different temperatures. The rate constants at 20°, 28°, and 35.5°C and $[\text{Mnbipy}^{2+}] = [\text{K}_3\text{Co}(\text{C}_2\text{O}_4)_3] = 10^{-3} \text{ mol dm}^{-3}$ came out to be 5.35×10^{-4} , 7.4×10^{-4} and $1.07 \times 10^{-3} \text{ s}^{-1}$ respectively. The system obeyed the Arrhenius equation. The values of E_a , A , $\Delta H^\ddagger$, $\Delta G^\ddagger$ and $\Delta S^\ddagger$ were evaluated as $34.02 \text{ kJ mol}^{-1}$, $1.2 \times 10^{-3} \text{ s}^{-1}$, $31.51 \text{ kJ mol}^{-1}$, $92.42 \text{ kJ mol}^{-1}$ and $-202.86 \text{ JK}^{-1} \text{ mol}^{-1}$ respectively. Within the experimental errors, similar values of the activation parameters were obtained at $[\text{K}_3\text{Co}(\text{C}_2\text{O}_4)_3] = 10^{-3} \text{ mol dm}^{-3}$ and $[\text{Mnbipy}^{2+}] = 3 \times 10^{-3} \text{ mol dm}^{-3}$.

The composition of the complex formed between Mnbipy^{2+} and $[\text{Co}(\text{C}_2\text{O}_4)_3]^{3-}$ applying Mauser's method^{6,7} (Fig. 1) and Yoe-Jones⁸ method was found to be 1:1 irrespective of $[\text{Mnbipy}^{2+}]$.

Finally using different concentration ratios of the reactants it was observed that the rate constant increased with increase in $[\text{Mnbipy}^{2+}]$ in the pres-

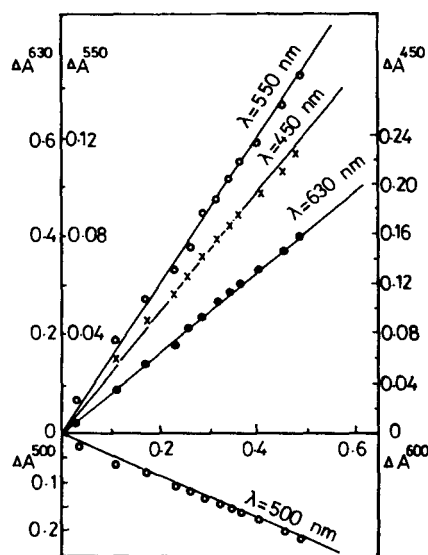


Fig. 1— ΔA diagram for $\text{K}_3[\text{Co}(\text{C}_2\text{O}_4)_3]$ and $[\text{Mnbipy}]^{2+}$ reaction

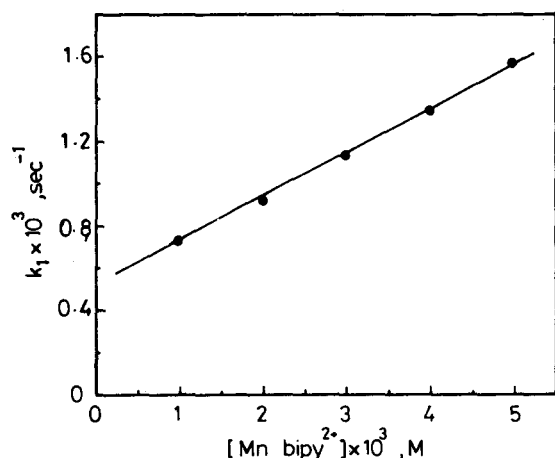
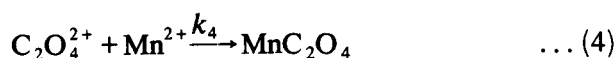
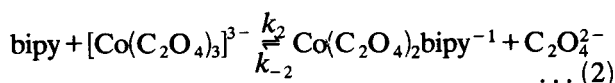
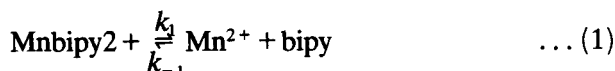


Fig. 2—Variation of k_1 with increasing $[\text{Mn bipy}^{2+}]$ at 28°C

ence of large excess of MnCl_2 used to diminish the presence of free bipyridyl (Fig. 2). This behaviour is opposite to that observed on adding bipyridyl only to the $\text{K}_3[\text{Co}(\text{C}_2\text{O}_4)_3]$ complex⁴.

On the basis of observation recorded above, a mechanism shown in Scheme 1 can be suggested for the ligand substitution reaction⁹.



Scheme 1

Based on Scheme 1 the rate-law (5) can be derived:

$$v = k_2[\text{bipy}][\text{Co}(\text{C}_2\text{O}_4)_3]^{3-} = k_3[\text{C}_2\text{O}_4^{2-}][\text{Mnbipy}^{2+}] \quad \dots (5)$$

The above mechanism is supported by the following observations:

- (i) First order kinetics in [trioxalate] at 600 nm. The formation of mixed ligand complex $[\text{Co}(\text{C}_2\text{O}_4)_2\text{bipy}]$ is an accepted fact since it has been synthesized and characterized spectrophotometrically¹⁰.
- (ii) Reaction rate increases with increase in $[\text{Mnbipy}^{2+}]$.
- (iii) Similar values of activation parameters obtained irrespective of reactant concentration ratios suggest the formation of only one activated complex. Also, Mouser's method sustains only one linear independent reaction (Fig. 1).
- (iv) High negative $\Delta S^\ddagger (= -202.86 \text{ JK}^{-1} \text{ mol}^{-1})$ confirms that the activated complex $[\text{Co}(\text{C}_2\text{O}_4)_3\text{bipy}]^{1-}$ results from $\text{Co}(\text{C}_2\text{O}_4)_3^{3-}$ in accordance with the extended Hückel theory¹¹.

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