Kinetics and Mechanism of the Oxidation of Formate and Malonate with (*trans*-1,2-Cyclohexanediamine-*N,N,N′,N′*-tetraacetato)manganate(III) in Aqueous Medium

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The kinetics of the reduction of (*trans*-1,2-cyclohexanediamine-*N,N,N′,N′*-tetracetato)manganate(III) by formate and malonate have been investigated in the pH regions 3.6—5.25 and 4.5—8.30 respectively at constant ionic strength and temperature. In the oxidation of formate slight initial increase in absorbance was observed, whereas for malonate oxidation no such indication was noted. Both the reactions are overall second-order with first-order on both the oxidant and reductants. A general rate law for the oxidation of formate and malonate can be given as $-d[\text{oxidant}]/dt = k[\text{oxidant}]\times[\text{reductant}]$, where k is the electron-transfer rate constant. The reactivity of $HCOO^-$ is $(3.26\pm0.16)\times10^{-5}$ dm^3 mol^{-1} s^{-1} (kK') and that of $Hmal^-$ and mal^{2-} are $(4.28\pm0.12)\times10^{-5}$ (k_1) and $(6.05\pm0.12)\times10^{-4}$ (k_2) dm^3 mol^{-1} s^{-1} respectively at 40 °C. A plausible inner-sphere mechanism has been suggested for the formate oxidation, whereas malonate oxidation has been interpreted by an outer-sphere mechanism.

The redox interactions involving manganese(III)/(II) couple have received much attention owing to the manganese dependent oxygen evolution in green plants and also that the chemical understanding of manganese should provide useful insight to the functional role of it in various biological systems.1) On the other hand, the oxidative decarboxylation of formate is of significant interest because of its relevance to the plant metabolism. A number of plant leaves readily catalyze the oxidation of formate to carbon dioxide which can be fixed photosynthetically.2,3) The reactions of malonic acid with a variety of oxidants4—9) also showed versatile mechanistic features.

The present report deals with the kinetics and mechanism of the oxidation of formate with a stable manganese(III) species, (*trans*-1,2-cyclohexanediamine-*N,N,N′,N′*-tetraacetato)manganate(III), $[Mn^{III}(cdta)]^-$. In addition, a comparable study with malonate pursues a wide pH range wherefrom the electron-transfer reactivities of $[Mn^{III}(cdta)(H_2O)]^-$ and $[Mn^{III}(cdta)(OH)]^{2-}$ can be inferred. The corresponding literature on $[Mn^{III}(cdta)]^-$ and oxalate reaction does not comment on this aspect.10) Inclusion of several forms of malonic acid (protonated and deprotonated) again substantially broadens the range of observed reactivities.

Experimental

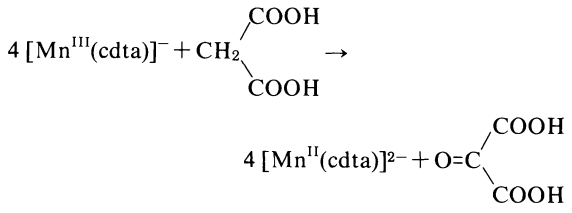
Materials and Reagents. The potassium salt of manganese(III) complex of *trans*-1,2-cyclohexanediamine-*N,N,N′,N′*-tetraacetic acid, $K[Mn^{III}(cdta)]\cdot2.5H_2O$ was prepared by the literature method.11) The purity of the complex was checked by elemental assay, spectrophotometric analysis, and also by iodometric titration. Malonic acid (E. Merck) and sodium formate (E. Merck) were of reagent grade and were recrystallized twice before use. Sodium perchlorate (Fluka AG) was recrystallized and used to maintain the ionic strength of the solution. Reagent grade AcOH–NaOAc, $NaBO_2$–NaOH were used as buffers to maintain the pH of the solution as required. All the solutions were freshly prepared in double-distilled water. Dissolved oxygen has no observable effect on the reaction rates.

Kinetic Measurements. Kinetics of the reactions were followed in a Pye-Unicam SP8-150 spectrophotometer equipped with thermostated cell-compartments by monitoring the decrease in optical density at 510 nm for aqua-($[Mn^{III}(cdta)(H_2O)]^-$) and at 448 nm for hydroxo-($[Mn^{III}(cdta)(OH)]^{2-}$) species, of the complex. pH measurements were done in a Systronics digital pH meter (model 335, India).

Polymerization Studies. Both the reactions were tested for the generation of free radical during the course of reaction by the method reported earlier.12) The precipitation of white polymer of acrylonitrile indicates that both the reactions proceed through the generation of free radicals.

Stoichiometry and Reaction Products. The direct determination of stoichiometry for both the oxidation of formate and malonate with $[Mn^{III}(cdta)]^-$ was not possible owing to the slowness of the reactions and occurrence of autodecomposition of the complex. But their product analyses were carried out very carefully in order to shed some light on the stoichiometries. For the oxidation of formate the product was carbon dioxide as tested by the usual method. For the analysis of the product in the oxidation of malonic acid, equimolar concentrations of $[Mn^{III}(cdta)]^-$ and reducing agent (0.05 mol dm^{-3}) were reacted. After the completion of the reaction, the organic product was extracted with diethyl ether. The ethereal extract also contained formaldehyde, the decomposition product of the complex.11) The extract was then washed with water, dried with anhydrous Na_2SO_4 and finally evaporated to dryness under high vacuum when formaldehyde was removed. The dry mass was then refluxed with equimolar quantity of *o*-phenylenediamine in a minimum volume of dry ethanol for an hour.13) The solid residue left after concentration of the product and cooling overnight in deep freeze was collected and recrystallized from anhydrous ethanol and then dried in a desiccator. The melting point, 266.3 °C, is identical to that of 2-hydroxy-3-isoquinoxalinecarboxylic acid14) obtained from the condensation of mesoxalic acid with *o*-phenylenediamine. Mesoxalic acid was also obtained in many oxidations of malonic acid where a 4 : 1 stoichiometry with respect to oxidant was found.15,16) The product (after extraction and drying in vacuum) also showed a positive 2,4-dinitrophenylhydrazine test. So the stoichiometric equations for the oxidation of formate and malonate can be represented as

$$2\,[\mathrm{Mn^{III}(cdta)}]^- + \mathrm{HCOO^-} \rightarrow 2\,[\mathrm{Mn^{II}(cdta)}]^{2-} + \mathrm{CO_2} + \mathrm{H^+}$$



$$4\,[\mathrm{Mn^{III}(cdta)}]^- + \mathrm{CH_2(COOH)_2} \rightarrow 4\,[\mathrm{Mn^{II}(cdta)}]^{2-} + \mathrm{O{=}C(COOH)_2}$$

Results and Discussion

Spectral scanning for the oxidation of formate by $[\mathrm{Mn^{III}(cdta)}]^-$ gives a very small initial increase in optical density having $[\mathrm{Mn^{III}(cdta)^-}]=5.0\times10^{-3}$ mol dm^{-3}, and [Formate]=1.00 mol dm^{-3} at pH 4.50 indicating the formation of a precursor complex and this then transforms slowly to the product by an electron transfer process. It is difficult to follow the first step of the reaction owing to the very small change in absorbance ($\Delta\varepsilon_{510}\approx2$ dm^3 mol^{-1} cm^{-1}). The corresponding reaction with an excess of malonate does not show the existence of such associated species.

The redox interactions of formate and malonate with $[\mathrm{Mn^{III}(cdta)}]^-$ were carried out in the range of pH 3.60—8.30 with variable concentrations of the reductants at constant ionic strength and temperature. When pseudo-first-order conditions are adopted, plots of $-\log(A_t-A_\infty)$ vs. t (all the signs have their usual significance) were all linear upto 85%, of the total reaction, indicating a first-order dependence of rate on oxidant. Plots of k_{obs} vs. [R] (where R represents the reductant) are all linear with a positive intercept on the rate axis conforming to a first-order dependence of rate on reductant, and intercept on the rate axis manifests an autodecomposition rate (k_d) of the complex. The corresponding data are listed in Table 1. Thus the general rate law for both the reactions is

$$-1/n\,\mathrm{d[ox]}/\mathrm{d}t=(k_\mathrm{d}+k_\mathrm{s}[\mathrm{R}])[\mathrm{ox}]=k_{\mathrm{obs}}[\mathrm{ox}], \tag{1}$$

where k_s=electron-transfer rate and n is the stoichiometric factor which is 2 for formate and 4 for malonate oxidation.

The effect of acidity on the rate of oxidation of formate was studied in the range of pH 3.60—5.25 with $[\mathrm{Mn^{III}(cdta)^-}]=1.0\times10^{-3}$ mol dm^{-3}, [formate]=1.0 mol dm^{-3} and I=1.10 mol dm^{-3} (NaClO$_4$) and temperature 40 °C. A plot of k_{ox} (where $k_{\mathrm{ox}}=(k_{\mathrm{obs}}-k_\mathrm{d})/2$[formate]) vs. $[\mathrm{H^+}]^{-1}$ is a limiting curve of decreasing slope with a nearly zero intercept on the rate axis (Fig. 1). This indicates that the molecular form of the acid is unreactive towards the complex. Thus, the observed rate constant may be given as

$$k_{\mathrm{ox}}=kK/(K+[\mathrm{H^+}]). \tag{2}$$

The pK of formic acid[17] is reported to be 3.90 and in the pH range 3.60—5.25, both the molecular and anionic forms of formic acid and only the aqua form of the

Table 1. Kinetic Data at Different Reductant Concentrations for the Oxidation of Formate and Malonate by $[\mathrm{Mn^{III}(cdta)}]^-$ at Different pH with $[\mathrm{Mn^{III}(cdta)^-}]=1.0\times10^{-3}$ mol dm^{-3} at 40 °C

Reductant	[Reductant]	pH	$10^4\,k_{\mathrm{obs}}/\mathrm{s^{-1}}$	
	mol dm^{-3}		5.0	8.0
Formate[a)]	0.20		0.33	
	0.50		0.53	
	0.80		0.73	
	0.90		0.79	
	1.00		0.84	
	1.10		0.91	
Malonate[b)]	0.07		0.70	2.54
	0.10		0.91	3.00
	0.30		2.31	5.68
	0.50		3.72	8.37
	0.70		5.12	11.05

a) I=1.10 mol dm^{-3}; $k_\mathrm{s}=(6.42\pm0.10)\times10^{-5}$ dm^3 mol^{-1} s^{-1} (slope); $k_\mathrm{d}=(2.06\pm0.08)\times10^{-5}$ s^{-1} (intercept). b) I=1.00 mol dm^{-3}; $k_\mathrm{s}=(7.02\pm0.05)\times10^{-4}$ dm^3 mol^{-1} s^{-1}; $k_\mathrm{d}=(2.08\pm0.20)\times10^{-5}$ s^{-1} at pH 5.0, and $k_\mathrm{s}=(13.46\pm0.12)\times10^{-4}$ dm^3 mol^{-1} s^{-1}, $k_\mathrm{d}=(1.65\pm0.05)\times10^{-4}$ s^{-1} at pH 8.0.

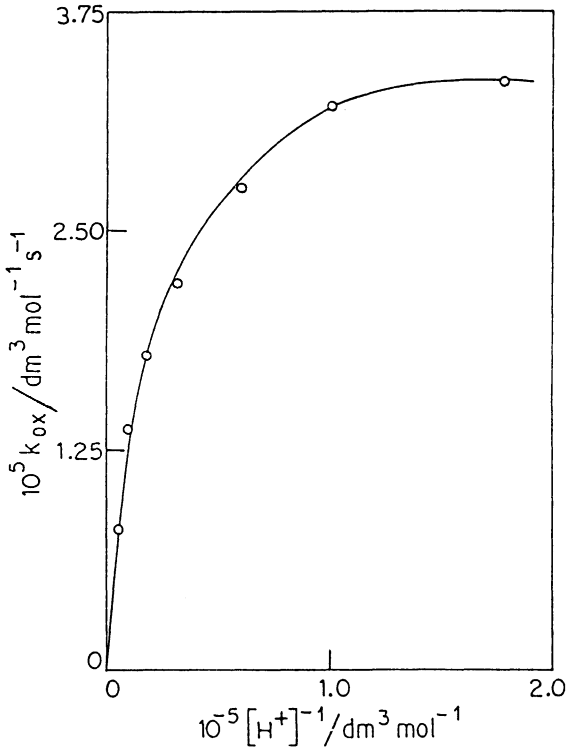


Fig. 1. A plot of k_{ox} vs. $[\mathrm{H^+}]^{-1}$ for the oxidation of formate with $[\mathrm{Mn^{III}(cdta)}]^-$ at [formate]=1.0 mol dm^{-3}, $[\mathrm{Mn^{III}(cdta)^-}]=1.0\times10^{-3}$ mol dm^{-3}, I=1.10 mol dm^{-3} (NaClO$_4$) and temperature 40 °C.

complex exist. An inner-sphere reaction scheme for the oxidation of formate anion by $[Mn(cdta)(H_2O)]^-$ can be depicted as

$$HCOOH \overset{K}{\rightleftarrows} HCOO^- + H^+ \tag{3}$$

$$[Mn^{III}(cdta)(H_2O)]^- + HCOO^- \overset{K'}{\rightleftarrows} [Mn^{II}(cdta)](HCOO)]^{2-} + H_2O \tag{4}$$

$$[Mn^{III}(cdta)(HCOO)]^{2-} \xrightarrow{k'} [Mn^{II}(cdta)]^{2-} + HCO\dot{O}^- \tag{5}$$

$$[Mn^{III}(cdta)(H_2O)]^- + HCO\dot{O} \xrightarrow{fast} [Mn^{II}(cdta)(H_2O)]^{2-} + CO_2 + H^+ \tag{6}$$

The complexation of $HCOO^-$ (Eq.4) is supported by the initial increase in absorbance. Here, $HCOO^-$ could be accomodated to the inner-sphere zone of $[Mn^{III}(cdta)(H_2O)]^-$ by the replacement of the coordinated water molecule or by partial opening of one of the carbonxylato arms of the hexadentate cdta moiety.[18,19] Accordingly a rate saturation should be obtained at high formate concentration. However, we could not find such results and it may be due to the very small formation constant of the formato species. The rate expression corresponding to the above reaction scheme can be expressed as

$$k_{ox} = KK'k'/(K+[H^+]) \tag{7}$$

Eqs. 2 and 7 are identical with $k=k'K'$. A plot of k_{ox}^{-1} vs. $[H^+]$ yields a straight line with slope $=1/KK'k'$ and intercept$=1/K'k'$. Thus the values of $K'k'$ and K are evaluated to be $(3.26\pm0.16)\times10^{-5}$ $dm^3 mol^{-1} s^{-1}$ and $(8.02\pm0.16)\times10^{-5}$ $mol\,dm^{-3}$ ($pK=4.10$) respectively. There is a reasonable agreement between the reported and kinetically determined value of pK for formic acid.

For the oxidation of malonic acid, the dependence of rate on $[H^+]$ was investigated in the range of pH 4.50—8.30 keeping $[Mn^{III}(cdta)^-]=1.0\times10^{-3}$ $mol\,dm^{-3}$, $[H_2mal]=0.50$ $mol\,dm^{-3}$, $I=1.00$ $mol\,dm^{-3}$ ($NaClO_4$) and temperature 40 °C. A plot of k_{ox} (where $k_{ox}=(k_{obs}-k_d)/4[H_2mal]$) vs. pH shows an initial increase in rate with pH, which reaches a maximum around pH 6.75 and then decreases yielding a bell-shaped curve (Fig. 2). This type of behavior could be obtained only when both the reactants are in protic equlibria, and only one form of one of the reactants reacts with both the protonated and deprotonated forms of the other.[20] The rate expression corresponding to such observation can be given as

$$k_{ox} = \frac{a+b[H^+]}{c+[H^+]}\left\{\frac{[H^+]}{d+[H^+]}\right\} \tag{8}$$

The proton dissociation of the complex[11] is given as

$$[Mn^{III}(cdta)(H_2O)]^- \overset{K_m}{\rightleftarrows} [Mn^{III}(cdta)(OH)]^{2-} + H^+,\ pK_m = 8.11 \tag{9}$$

and that of H_2mal[17] as

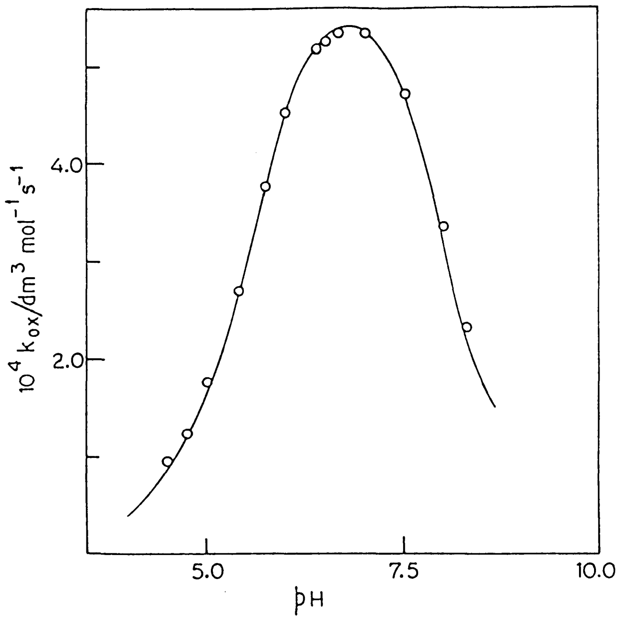


Fig. 2. A pH–rate profile for the oxidation of malonate by $[Mn^{III}(cdta)]^-$ at $[malonate]=0.50$ $mol\,dm^{-3}$, $[Mn^{III}(cdta)^-]=1.0\times10^{-3}$ $mol\,dm^{-3}$, $I=1.0$ $mol\,dm^{-3}$ ($NaClO_4$) and temperature 40 °C. The solid line represents the theoretical curve and points, the experimental values.

$$H_2mal \overset{K_1}{\rightleftarrows} Hmal^- + H^+;\ pK_1 = 2.88 \tag{10}$$

$$Hmal^- \overset{K_2}{\rightleftarrows} mal^{2-} + H^+;\ pK_2 = 5.68 \tag{11}$$

In the range of pH 4.50—8.30, the reacting species of malonic acid are $Hmal^-$ and mal^{2-}. But above pH 6.0, the hydroxo form of the complex starts to prevail. Taking aqua form of the complex as the only reacting species, the following outer-sphere reaction scheme for the oxidation of malonic acid could be proposed.

$$[Mn^{III}(cdta)(H_2O)]^- + Hmal^- \xrightarrow{k_1} [Mn^{II}(cdta)(H_2O)]^{2-} + \text{free radical} \tag{12}$$

$$[Mn^{III}(cdta)(H_2O)]^- + mal^{2-} \xrightarrow{k_2} [Mn^{II}(cdta)(H_2O)]^{2-} + \text{free radical} \tag{13}$$

$$[Mn^{III}(cdta)(H_2O)]^- + \text{free radical} \xrightarrow{fast} [Mn^{II}(cdta)(H_2O)]^{2-} + \text{products} \tag{14}$$

If the assumption is made that the reaction stoichiometry (4 : 1) is valid under the reaction conditions, the rate expression corresponding to the above reaction scheme takes the form

$$k_{obs} = 4\frac{k_2K_2 + k_2[H^+]}{K_2+[H^+]}[H_2mal]\left\{\frac{[H^+]}{K_m+[H^+]}\right\} \tag{15}$$

and

$$k_{ox} = \frac{k_2K_2 + k_1[H^+]}{K_2+[H^+]}\left\{\frac{[H^+]}{K_m+[H^+]}\right\} \tag{16}$$

Both Eqs. 8 and 16 are identical with $a=k_2K_2$, $b=k_1$, $c=K_2$, and $d=K_m$.

Experimental data were fitted to Eq. 16 by means of a Simplex Optimization program. Best fit of data was obtained by allowing K_2 and K_m to vary and the corresponding values of the parameters evaluated to be: $k_1=(4.28\pm0.12)\times10^{-5}$ dm^3 mol^{-1} s^{-1} and $k_2=(6.05\pm0.20)\times10^{-4}$ dm^3 mol^{-1} s^{-1} and $K_2=(2.52\pm0.07)\times10^{-6}$ mol dm^{-3} (pK_2=5.60) and $K_m=(8.14\pm0.25)\times10^{-9}$ mol dm^{-3} (pK_m=8.09). There is an excellent agreement between the calculated and reported values of pK of malonic acid and complex. There is also an agreement between the experimental and calculated k_{ox} values (Fig. 2) and this supports the proposed mechanism.

The reduction of $[Mn^{III}(cdta)]^-$ with formate and malonate seems interesting owing to their different modes of reaction. Previously, the redox interaction of $[Mn^{III}(cdta)]^-$ with several organic and inorganic reagents have been investigated mainly in the acidic medium.[21–30] However, very little is known about the redox behavior of the corresponding hydroxo form of the complex. Few reports in the literature comprise the redox behavior of the complex in the alkaline medium.[31,32] Most of the reactions of $[Mn^{III}(cdta)]^-$ are believed to proceed through inner-sphere pathways[21–30] barring a few reports going through outer-sphere route.[10,31,32] In the oxidation of formate, a distinct evidence in favor of inner-sphere mechanism comes from the initial increase in absorbance. This probaly occurs due to the coordination of $HCOO^-$ through the displacement of water molecule from the inner coordination zone of $[Mn^{III}(cdta)(H_2O)]^-$. This then undergoes the electron-transfer process unimolecularly. The reduction potential values of HCOOH and $HCOO^-$ are −0.14 and −0.25 V respectively.[33] The formate anion is the only reactive species leaving the corresponding molecular form unreactive towards the complex. This could be explained by the more negative value of reduction potential of $HCOO^-$. In the oxidation of malonate no spectral or kinetic evidence lends support for inner-sphere process. Most of the reactions of malonic acid are inner-sphere type[4–9]. Only in the oxidation of malonic acid by $CoW_{12}O_{40}^{5-}$ [E°=1.0 V][34] and $IrCl_6^{2-}$ [E°=1.021 V][35] an outer-sphere mechanism was suggested.[16,36] In order to correlate these rate data with the present investigation we calculated the reactivity of $Hmal^-(k_1)$ towards $CoW_{12}O_{40}^{5-}$ and $IrCl_6^{2-}$ at 40 °C and I= 1.0 mol dm^{-3} from the reported data at different temperatures. The evaluated values are 7.94×10^{-4} and 3.75×10^{-3} dm^3 mol^{-1} s^{-1} respectively for $CoW_{12}O_{40}^{5-}$ and $IrCl_6^{2-}$. A good linearity is observed for a plot of log k vs. E° for these systems with a slope 8.20±2.15 V^{-1}. Marcus predicted[37] that for outer-sphere reactions slope for such a plot should be 8.5 V^{-1}. It is apparent from the slope value that our results show a good qualitative agreement with the Marcus theory. Oxidation of oxalate by $[Mn^{III}(cdta)]^-$ also serves as an example for outer-sphere mechanism.[10] The steric factor of the larger oxalate and malonate groups probably inhibit the inner-sphere association and leads the reactions to proceed through an outer-sphere route. Comparison of rate shows that mal^{2-} (k_2) is 14 times more reactive than $Hmal^-$ (k_1). The decrease in rate with pH (after attainment of the maximum) is associated with the deprotonation of the coordinated water molecule in $[Mn^{III}(cdta)(H_2O)]^-$(pK_m=8.11) resulting in the decrease in reduction potential,[32,38] and this makes the hydroxo species unreactive towards malonate. Similar observations were also made in the oxidation of some inorganic reagents and complexes where an outer-sphere mechanism was proposed.[32,39,40]

The autodecomposition rate of $[Mn^{III}(cdta)(H_2O)]^-$ and $[Mn^{III}(cdta)(OH)]^{2-}$ were determined from the intercept of the plot of k_{obs} vs. [R] at 40 °C (Table 1). These are in well agreement with the values obtained in the oxidation of histidine[41] (k_d=1.93 $\times10^{-5}$ s^{-1} in the acid medium and 1.61×10^{-4} s^{-1} in the alkaline medium at 40 °C).

References

1) G. D. Lawrence and D. T. Sawyer, *Coord. Chem. Rev.*, **27**, 173 (1978), and the references therein.

2) J. Halliwell, *Biochem. J.*, **138**, 177 (1974).

3) E. R. Still and P. Wikberg, *Inorg. Chim. Acta*, **46**, 153 (1980).

4) Z. Amjad and A. McAuley, *J. Chem. Soc., Dalton Trans.*, **1977**, 304.

5) J. Jwo and R. M. Noyes, *J. Am. Chem. Soc.*, **97**, 5422 (1975).

6) B. S. Maritz and R. van Eldik, *Inorg. Chim. Acta*, **20**, 43 (1976).

7) F. Mata and M. P. Alvarez, *Z. Phys. Chem. (Frankfurt)*, **120**, 155 (1980).

8) K. K. Sengupta and A. K. Chatterjee, *Z. Phys. Chem. (Frankfurt)*, **75**, 15 (1971).

9) A. Y. Drummond and W. A. Waters, *J. Chem. Soc.*, **1954**, 2456.

10) M. A. Suwyn and R. E. Hamm, *Inorg. Chem.*, **6**, 142 (1967).

11) R. E. Hamm and M. A. Suwyn. *Inorg. Chem.*, **6**, 139 (1967).

12) M. Ali, S. K. Saha, and P. Banerjee, *J. Chem. Soc., Dalton Trans.*, **1990**, 187.

13) A. O. Fitton and R. K. Smalley, "Practical Heterocyclic Chemistry," Academic Press, London(1968), p. 108.

14) Eyre and Spottiswoode, "Dictionary of Organic Compounds," (1953),Vol. 1, p. 262.

15) G. Calvaruso. A. I. Carbone, and F. Cavasino, *J. Chem. Soc., Dalton Trans.*, **1985**, 1683.

16) S. K. Saha, M. C. Ghosh, and P. Banerjee, 4th International Conference on Mechanism of Reactions in Solution, The University of Kent at Canterbury, U. K., 1986, Abstr., p. 18.

17) L. G. Sillen and A. E. Martel, in "Stability Constant of Metal-Ion Complexes," The Chemical Society, London (1964), Special Publ. No. 17, pp. 357 and 385.

18) G. Giraudi and E. Mentasti, *Transition Met. Chem.*, **4**, 230 (1981).

19) E. Mentasti, *J. Chem. Soc., Dalton Trans.*, **1982**, 721.

20) R. G. Wilkins,"The Study of Kinetics and Mechanism of Reactions of Transition Metal Complexes," 1974, p. 47.

21) D. J. Boone, R. E. Hamm, and J. P. Hunt, *Inorg. Chem.*, **11**, 1060 (1972).

22) T. E. Jones and R. E. Hamm, *Inorg. Chem.*, **13**, 1940 (1974).

23) W. H. Woodruff and D. W. Margerum, *Inorg. Chem.*, **13**, 2578 (1975).

24) T. E. Jones and R. E. Hamm, *Inorg. Chem.*, **14**, 1027 (1975).

25) J. Stein, J. P. Facker, Jr., G. J. MacCline, J. A. Fee, and L. T. Chan, *Inorg. Chem.*, **18**, 3511 (1979).

26) P. Arselli and E. Mentasti, *J. Chem. Soc., Dalton Trans.*, **1983,** 689.

27) V. M. Bobba, G. Giraudi, and E. Mentasti, *Transition Met. Chem.*, **13**, 256 (1988).

28) S. Gangopadhyay, S. K. Saha, M. Ali, and P. Banerjee, *Int. J. Chem. Kinet.*, **23**, 105 (1990).

29) M. A. Suwyn and R. E. Hamm, *Inorg. Chem.*, **6**, 2150 (1967).

30) S. Gangopadhyay, S. K. Saha, and P. Banerjee, *Transition Met. Chem.*, **16**, 355 (1991).

31) R. G. Wilkins and R. E. Yelin, *Inorg. Chem.*, **7**, 2667 (1968).

32) D. H. Macartney and D. W. Thompson, *Inorg. Chem.*, **28**, 2195 (1989).

33) S. K. Saha, M. C. Ghosh, and P. Banerjee, *Inorg. Chim. Acta*, **126**, 26 (1986).

34) L. Eberson, *J. Am. Chem. Soc.*, **105**, 3192 (1983).

35) S. C. Woo, *J. Am. Chem. Soc.*, **53**, 469 (1931).

36) G. Calvaruso, A. I. Carbone, and F. P. Cavasino, *J. Chem. Soc., Dalton Trans.*, **1985**, 1683.

37) R. A. Marcus, *J. Chem. Phys.*, **45**, 497, 2654(1965); R. A. Marcus, *J. Phys. Chem.*, **72**, 891 (1968).

38) A. Chakravorty, *Comments Inorg. Chem.*, **4**, 1 (1985).

39) I. K. Adzamli, D. M. Davies, C. S. Stanley, and A. G. Sykes, *J. Am. Chem. Soc.*, **103**, 5543 (1981).

40) S. Gangopadhyay, M. Ali, S. K. Saha, and P. Banerjee, *J. Chem. Soc., Dalton Trans.*, **1991**, 2729.

41) S. Gangopadhyay, M. Ali, and P. Banerjee, unpublished work.