THE KINETICS AND MECHANISMS OF SUBSTITUTION REACTIONS OF TRANS-[Co(en)$_2$CNCl]$^+$ IN BINARY MIXED SOLVENT

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ABSTRACT: *The kinetics and mechanisms of the substitution reactions of trans-[Co(en)$_2$CNCl]$^+$ with unidentate anions, NO_2^-, CN^-, I^-, N_3^-, Br^-, and SCN^- in 60% v/v DMF-H$_2$O binary solvent at 40.0±0.2°C were studied spectrophotometrically. An I_d mechanism was assigned for the replacement of chlorine by NO_2^-, CN^-, and I^-, an I_a one for the entry of N_3^- and SCN^-, and a D mechanism for Br^- entry. Comparing the interchange rate constants, k_i, values has led to the following trend of reactivity of the anions toward the given substrate:*

$$NO_2^- > N_3^- > Br^- > CN^- > H_2O > I^- > SCN^-$$

The replacement of chlorine by the anions proceeded with a complete retention of configuration.

KEY WORDS: *Mixed solvents, Substitution reactions, Co(III) Complexes, Kinetics, Mechanism, Anion interchanges*

INTRODUCTION

The replacement of one unidentate ligand by another is the simplest substitution which is used to explain the mechanism of substitution in octahedral Co(III) complexes [1]. Most of the data reported to date, have been on reactions carried out in aqueous solutions [2,3]. The involvement of a water molecule in the transition state as a weakly bonded nucleophile is still debatable [4].

In the present work the substitution reactions between *trans*-[Co(en)$_2$CNCl]$^+$ and various anions, CN$^-$, NO$_2^-$, N$_3^-$, SCN$^-$, I$^-$, and Br$^-$ in binary 60% v/v DMF-H$_2$O solvent at 40°C are studied by spectrophotometric techniques.

EXPERIMENTAL

Dimethylformamide solvent of analytical grade obtained from Merck. Inorganic chemicals of Analar grade were used without further purification, except for potassium cyanide (Merck) which was recrystallized before use. Ethylenediamine, cobalt chloride
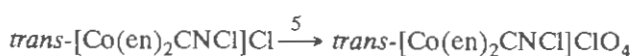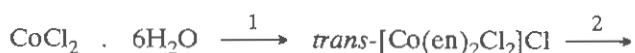
six hydrate, hydrochloric acid, hydrogen peroxide, sodium sulfite, methanol, ether, sodium perchlorate were obtained from Fluka and used without further treatment.

Preparation of Co(III) complexes

The complex *trans*-[Co(en)$_2$CNCl]ClO$_4$ was prepared by the following reactions:

$$CoCl_2 \; . \; 6H_2O \xrightarrow{\;1\;} trans\text{-}[Co(en)_2Cl_2]Cl \xrightarrow{\;2\;}$$

$$[Co(en)_2Cl(SO_3)] \xrightarrow{\;3\;} [Co(en)_2(SO_3)CN] \xrightarrow{\;4\;}$$

$$trans\text{-}[Co(en)_2CNCl]Cl \xrightarrow{\;5\;} trans\text{-}[Co(en)_2CNCl]ClO_4$$

Trans-[Co(en)$_2$Cl$_2$]Cl was prepared from CoCl$_2$. 6H$_2$O and ethylenediamine through oxidation by hydrogen peroxide (yield 70-87%) [5]. [Co(en)$_2$Cl-(SO$_3$)] was prepared according to Baldwin procedure [6]. [Co(en)$_2$CN(SO$_3$)] was prepared according to procedure cited in reference [6], by mixing equivalent amounts of KCN solution with [Co(en)$_2$(SO$_3$)Cl]. [Co(en)$_2$CNCl]ClO$_4$ was prepared by dissolving a given amount of [Co(en)$_2$(SO$_3$)Cl] in a minimum amount of concentrated hydrochloric acid, then by adding solid sodium perchlorate the crystals were precipitated [7], (yield 85-95%).

The infrared and the visible absorption spectra of the prepared complexes were in accord with those reported in the literature [6,7].

Spectroscopic techniques

Visible and ultraviolet spectra of the prepared Co(III) complexes were recorded on a PU 8750/Philips spectrophotometer.

The infrared spectra of the complexes were recorded on a Perkin-Elmer 781 spectrophotometer.

Kinetic studies

Since all the reactions studied are slow, their rates were followed by conventional spectrophotometric techniques. The temperature was kept constant at 40±0.2°C by a thermostated cell compartment of the spectrophotometer. The kinetics were followed at a pre-determined wavelength at which a maximum difference between the spectrum of the substrate and the product was observed in an earlier "trial run"

experiment [8]. The kinetics were followed in the presence of excess of a given nucleophile to ensure pseudo first-order kinetics. Binary mixed solvent of 60% v/v DMF-H$_2$O was used. The absorbance was measured at definite intervals without disturbing the reaction mixtures in a stoppered spectrophotometric cell. Ionic strengths were maintained constant for each reaction by adding proper amounts of dried NaClO$_4$. The visible spectra of the reaction solution on attainment of equilibrium were closely similar to those of the expected *trans*-products.

General method

The kinetics of the substitution reactions (1):

$$trans\text{-}[Co(en)_2CNCl]^+ + Y^- \longrightarrow$$
$$trans\text{-}[Co(en)_2CNY]^+ + Cl^- \tag{1}$$
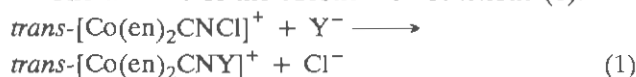
have been studied by spectrophotometry. The nucleophiles Y$^-$ include SCN$^-$, Br$^-$, I$^-$, N$_3^-$, NO$_2^-$, and CN$^-$. The close similarity of the expected product spectrum and the spectrum of the reaction mixture at equilibrium indicates that under the excess Y$^-$ concentration, the substitution is effectively complete. The data obtained in this work have been treated by a non-linear least squares program fitted to the Eq. (2):

$$A_t = (A_o - A_{oo}) e^{-kt} + A_{oo} \tag{2}$$

The observed rate constants were calculated by using Quick Basic computer application. The standared deviation of an individual rate constant is within the standard error of ±4%. Plotting k$_{obs}$ against the initial nucleophile concentration for all the reactions studied in binary mixed 50% v/v DMF-H$_2$O as solvent, show one of the three general patterns shown in Fig. 1. The experimental kinetic results are shown in Table 1 and in Fig. 2.
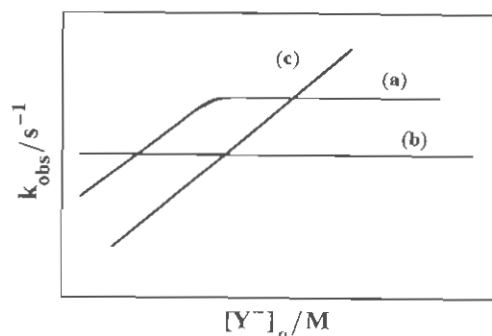

Fig. 1: Dependence of pseudo-first-order rate constant, k_{obs} upon Y$^-$ concentration.

Table 1: The kinetic data for the reaction of trans-[Co(en)$_2$CNCl]$^+$ with various nucleophiles in 60% v/v DMF/H$_2$O solvent at 40±0.2°C and in various ionic strengths

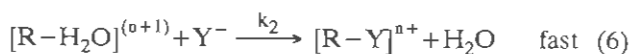|								
KSCN(10^2M)	12.1	22.8	35.1	45.6	78.7	91.2		
10^6K$_{obs}$(s^{-1})	4.65	5.12	5.37	5.96	7.20	7.82		
KN$_3$[10^2M]	3.36	3.74	5.51	7.12	7.48	7.95		
10^4K$_{obs}$(s^{-1})	0.92	0.98	1.21	1.39	1.42	1.52		
KBr(10^2M)	13.7	18.2	31.9	45.6	57.6	68.4		
10^4K$_{obs}$(s^{-1})	1.56	1.62	1.53	1.58	1.55	1.54		
KI(10^2M)	4.56	13.7	22.8	45.6	63.8	91.2		
10^6K$_{obs}$(s^{-1})	3.59	5.59	6.61	6.68	9.83	9.87		
KNO$_2$(10^2M)	9.1	13.7	18.2	22.8	45.6	63.3	91.2	
10^4K$_{obs}$(s^{-1})	1.61	3.70	5.05	5.38	6.68	7.02	7.20	
KCN(10^2M)	0.92	1.72	2.73	3.64	4.56	6.38	9.12	10.09	13.68
10^4K$_{obs}$(s^{-1})	2.25	2.44	3.24	4.71	5.25	5.70	5.78	5.79	5.98
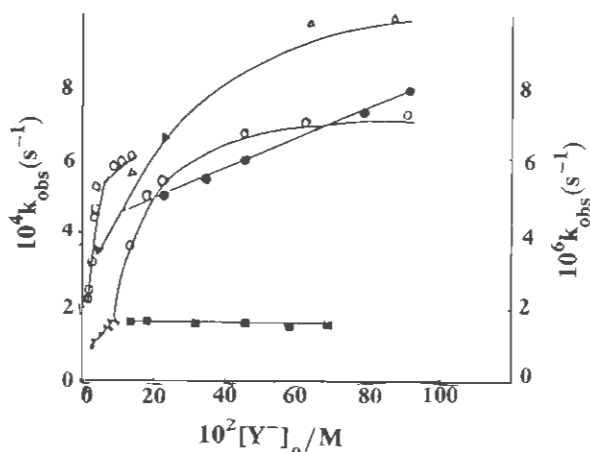
Fig. 2: Dependence of K$_{obs}$ upon the nuclcophile concentration, left: o, NO$_2^-$; □, CN$^-$; ■, Br$^-$; ∇, N$_3^-$; right: ●, SCN$^-$; △, I$^-$

RESULTS AND DISCUSSION

Reactions which follow pattern (I$_d$), Fig. 1 are best explained in terms of the rate law derived by *Schiavan* et al. [9] were found to best fit our experimental data, (Eq. 7), for the reactions with I$^-$, NO$_2^-$, and CN$^-$ ions.

$$[R-X]^{n+} + Y^- \overset{K}{\rightleftharpoons} [R-X]^{n+} \dots\dots Y^- \qquad \text{fast (3)}$$

$$[R-X]^{n+} \dots\dots Y^- \xrightarrow[\text{r.d.s.}]{k_i} [R-Y]^{n+} + X^- \qquad \text{slow (4)}$$

$$[R-X]^{n+} + H_2O \overset{k_0}{\underset{k_1}{\rightleftharpoons}} [R-H_2O]^{(n+1)+} + X^- \quad \text{slow (5)}$$

$$[R-H_2O]^{(n+1)} + Y^- \xrightarrow{k_2} [R-Y]^{n+} + H_2O \qquad \text{fast (6)}$$
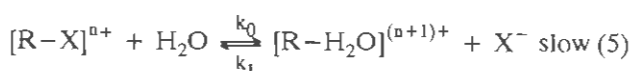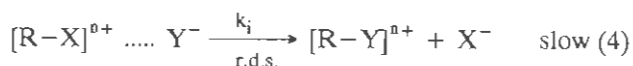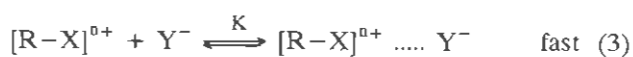
$$k_{obs} = \frac{k_i K[Y^-]_o + k_o}{1 + K[Y^-]_o} \qquad (7)$$

Plotting the inverse of Eq. (7) yields a straight line (Eq. 8) from which the interchange rate constant of the ion-pair k$_i$ and the ion-pair association constant, K can be estimated, provided k$_o$ is known from the zero concentration intercept of the k$_{obs}$ vs [Y$^-$]$_o$ plots, (see Fig. 2.).

$$\frac{1}{k_{obs}} = \frac{1}{k_i - k_o} + \frac{1}{(k_i - k_o)K[Y^-]_o} \qquad (8)$$

Table 2 shows the estimated k$_i$ and K values for the systems studied.

Comparing the k$_i$ values in Table 2, the relative reactivity of the nucleophiles toward the substrate at 40°C is as follows:

NO$_2^-$ > N$_3^-$ > Br$^-$ > CN$^-$ > H$_2$O > I$^-$ > SCN$^-$

The activity of an anion mainly depends upon the degree of solvation [14] and basic strength [11]. k$_i$ values are independent of the ionic strength changes, as it is due to an intramolecular rearrangement. Therefore, a comparison of nucleophile reactivities could be made.

The entry rate of SCN$^-$ into the substrate is linearly dependent upon its concentration, which supports an I$_a$ mechanism. *Langford* et al. [12] found that the reaction of SCN$^-$ with *trans*-[Co(en)$_2$- NO$_2$Cl]$^+$ in binary water-dimethylformamide and in pure DMF is independent of SCN$^-$ concentration. It is obvious that -NO$_2$ or -CN as non-participating groups promote an I$_a$ mechanism. The work of *Asper-*

Table 2: Kinetic data for the substitution reactions of trans-[Co(en)$_2$CNCl]$^+$ with various nucleophiles, Y$^-$, at 40.0±0.2°C in 60% v/v DMF/H$_2$O solvent

Y$^-$	$k_i \times 10^{-6}$ (s^{-1})	K (M^{-1})	$\bar{k}_2{}^a \times 10^{-6}$ (M^{-1}s^{-1})	Ionic strength (M)	Mechanism suggested
SCN$^-$	7.4	12.3	1.8	0.95	$I_a(I_d)^c$
I$^-$	16	20.2	29.5	0.95	I_d
Br$^-$	156.5^b	—	560	0.70	D
NO$_2{}^-$	830	7.3	1900	0.95	$I_d(D)^c$
N$_3{}^-$	270	15.4	2220	0.50	$I_a(I_d)^c$
CN$^-$	120	13.2	11200	0.50	I_d
H$_2$O	82^d				$(D)^c$

a) $\bar{k}_2 = \dfrac{k_2}{n}$, $k_2 = \dfrac{k_{obs}}{[Y^-]_o}$

b) $\bar{k}_{obs} = \dfrac{k_{obs}}{n}$

c) The mechanism in parentheses is obtained by other investigators [2,8,10-13]

d) Acid hydrolysis of the complex quoted from ref. 2, P. 171, for comparison

ger et al. [13] in methanol has shown that the reaction of SCN$^-$ with *trans*-[Co(en)$_2$(NO$_2$)Cl]$^+$ follows an I_a mechanism. But with *trans*-[Co(en)$_2$CNCl]$^+$ follows an I_d one [8]. An I_a mechanism was obtained for the entry of SCN$^-$ into *trans*-[Co(en)$_2$(NO$_2$)H$_2$O]$^{2+}$ in mixed aqueous-tetramethylsulfone [15]. Also the entry of SCN$^-$ into *trans*-[Co(en)$_2$(NO$_2$)Br]$^+$ in water-sulpholane has shown to follow an I_a mechanism [16].

N$_3{}^-$ behaves like SCN$^-$ and follows an I_a mechanism (Table 1). The previous works in methanol [8] for the entry of N$_3{}^-$ into *trans*-[Co(en)$_2$CNCl]$^+$ showed an I_d mechanism. However, the enhanced rate of N$_3{}^-$ compared with SCN$^-$ is due to its higher basic strength [13,17].

The entry of NO$_2{}^-$, CN$^-$, and I$^-$ into the substrate *trans*-[Co(en)$_2$CNCl]$^+$ follow an I_d mechanism as the entry of NO$_2{}^-$ in methanol [8]. But the NO$_2{}^-$ reaction with *trans*-[Co(en)$_2$(NO$_2$)Cl]$^+$ in DMSO was explained on the basis of S$_N$1CB mechanism [18].

The entry of Br$^-$ into *trnas*-[Co(en)$_2$CNCl]$^+$ follows a D mechanism where the slow step is the aquation process. The previous works in methanol for the reaction of Br$^-$ with *cis*-[Co(en)$_2$H$_2$OCl]$^{2+}$ in the presence of HClO$_4$ showed a D mechanism [19]. Also the entry of Br$^-$ into *cis*-[Co(en)$_2$Cl$_2$]$^+$ in methanol followed a D mechanism [20].

Cyano-group in *trans*-[Co(en)$_2$CNCl]$^+$, like nitro-group promotes an A or I_a mechanism in the ligand substitution reactions, probably at somewhat reduced rate. The strong orientating effect of the cyano-group arises from the negative electromeric effect exerted on the 3d non-bonding shell of the cobalt atom. The group retards substitution in all positions but especially in those adjacent to itself. The polarization of cobalt should provide access to the entering anion. But the same polarization will oppose heterolysis of the departing chloride. The first effect to be expected of such electron displacement is an inhibition of anion attack in *cis*- position to the cyano-group, and hence an orientation of the attack towards the *trans*-position. Thus a predominating retention of configuration when the *trans*-chlorine is displaced has been observed.

What seems most significant, however, is the observation that the extrapolation of the specific replacement rates to zero reagent concentration gives a finite value for all anions except for Br$^-$ (which follows a D mechanism). These results seem to favor the bimolecular mechanism described through aquation pathway (k_o). According to this mechanism the activation energy is supplied from the complex-water bond formation and the cobalt-chlorine bond lengt-

hens, but not sufficiently to cause dissociation. The anion, Y^-, which is already in the solvation shell, could quickly enter the coordination shell.

The finite intercept at zero reagent concentration of the plots of k_{obs} versus $[Y^-]_o$ [patterns (I_d) and (I_a) in Fig. 1] support the idea that the replacement of chlorine by the anions, Y^-, requires a step through which the solvent molecule form a solvate intermediate (aqua intermediate), which is followed by a fast replacement of the coordinated solvent by the entering anion. *Asperger* and *Ingold* [21], suggested that 4d-orbitals of cobalt play an intermediate role in the binding of water, which is greatly assisted when the underlying 3d-shell is pulled out of the way by the cyano-group.

Since the activity of the anions are greater than water and DMF solvent molecules, therefore there is no chance for these solvent molecules to compete with the entering anions in the ion-pair outer-inner sphere interchange [22]. However, there is a good chance for water molecules as a hard base to replace the chloride ion with the hard free substrate, through formation of aqua intermediate. The most novel feature of this study was a radically altered competitive position for nucleophiles. The solvent DMF does not form a strong complex with the substrate and is therefore, of potentially lower nucleophilicity than water. It is known that the solvent plays a major role, not only in the magnitude of rate constants, but also in the orders of nucleophilic reactivity. As far as the entry of anions into ionic complexes in organic and mixed solvents is concerned, the nature of the solvent and its solvating power upon the complexes and the entering anions have to be considered [14]. Some of these solvents would form stable solvated intermediates with the complexes, which could be isolated easily from the reaction mixture. Unfortunately we were unable to isolate such intermediates in the present work. But the k_o pathway is a good evidence for such intermediates. Some of these intermediates are labile and could not be observed. The kinetics and related experimental evidence for some of these solvento complex intermediates have been reported in the literature [2].

However, the properties of a solvent are variable with respect to a range of complexes, i. e. each complex has certain characteristics in a given solvent,

but probably different behavior is found with respect to the anions [14]. Therefore, it is to be expected that the kinetics of substitution of one anionic ligand by another in mixed solvents will be more complicated than in aqueous solutions and hence simple rate laws are not common. The existence of ion-pair species in equilibrium with the free complex could be investigated qualitatively by observing the shift of the visible and near ultra-violet spectrum of the complex under investigation, and its association constant could be determined spectrophotometrically. The smaller values of the ion-pair formation constants of the *trans*-$[Co(cn)_2CNCl]^+$ with the anions, (see Table 2), obtained from the inverse plots of Eq. (8) indicate that binary DMF/H_2O, solvates anions even better than methanol does [18].

The general interpretation of these results is that there are specific solvation effects operating in different solvents, and these are not taken into account by any of the simple models. However, it is not widely aknowledged that these greatly weakens all of the more simplistic rationalizations that are used to explain the results of these types of studies. The aquation reaction is faster compared with direct entry of SCN^- and I^- ions into the substrate ion pair and thus it seems that aquation would necessarily precede those anions (Table 2).

ACKNOWLEDGEMENT

REFERENCES

[1] Margerum, D. W., Cayley, G. R., Weatherburn, D. C. and Pagenkopf, G. K., in B32, Chap. 1 (1977).

[2] Basolo, F. and Pearson, R. G., "Mechanisms of Inorganic Reactions", Wiley, New York, 2nd Ed., P. 158(1967).

[3] Sayell, D. M., Borman, C. D., Kwak, C. H. and Sykes, A. G., *Inorg. Chem.*, **35**, 173(1996).

[4] Dimmock, P. W., Lamprecht, G. J. and Sykes, A. G., *J. Chem. Soc. Dalton Trans.*, 955(1991).

[5] Levrett, P. and Oliver, M. J., *J. Chem. Educ.*, **53**,

440(1976).

[6] Baldwin, M. F., *J. Chem. Soc.,* 3123(1961).

[7] Chan, S.C. and Tobe, M. L., *J. Chem. Soc.,* 966 (1963).

[8] Bradic, Z., Birus, M., Pavlovic, D., Pribanic, M. and Asperger, S., *J. Chem. Soc. Dalton,* 2514 (1973).

[9] Schiavon, C. and Pavadisi, C., *Inorg. Chim. Acta,* **41,** 99(1980).

[10] Tobe, M. L., in "Mechanisms of Inorganic Reactions", Advances in Chemistry Series, Ed. R. F. Gould, No. 49, 7(1965).

[11] Pearson, R. G., Sobel, H. and Songstad, J., *J. Am. Chem. Soc.,* **90,** 319(1968).

[12] Langford, C. H. and Langford, P., *Inorg. Chem.,* **12,** 300(1963).

[13] Asperger, S., Pavlovic, D. and Orhanovic, M., *J. Chem. Soc.,* 2142(1961).

[14] Miller, J. and parker, A. J., *J. Am. Chem. Soc.,*

83, 117(1961).

[15] Langford, C. H. and Johnson, M. P., *J. Am. Chem. Soc.,* **86,** 229(1964).

[16] Langford, C. H., Thesis, Northwestern University, Evanston, Illinois (1960).

[17] Pearson, R. G., *J. Am. Chem. Soc.,* **85,** 3533 (1963).

[18] pearson, R. G., Schmidtke, H. H. and Basolo, F., *J. Am. Chem. Soc.,* **82,** 4434(1960).

[19] Asperger, S. and Flogel, M., *J. Chem. Soc.,* 769 (1968).

[20] Brown, D. D. and Ingold, C. K., *J. Chem. Soc.,* 2680(1953).

[21] Asperger, S. and Ingold, C. K., *J. Chem. Soc.,* 2862(1956).

[22] Langford, C. H. and Gray, H. B., "Lignad Substitution Processes", Benjamin, New York, P. 72 (1965).