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Kinetics and Mechanism of Substitution of Chloride Ion in *trans*-$[Co(en)_2Cl_2]^+$ by Organic Bases in Dimethyl Acetamide Solution

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The kinetics of substitution of chloride ion in *trans*-dichlorobis(ethylenediamine) cobalt(III) cation by five organic bases (diethylamine, triethylamine, benzylamine, *t*-butylamine and *n*-propylamine) in dimethylacetamide (DMA) at ionic strength of 0.80 M $NaClO_4$ is reported. The activation parameters for the second-order path lie on a good isokinetic line. The linear plots of k_{obs} *vs.* [B], the large negative values of $\Delta S_2^{\ddagger}$ and the span of k_2 values signify an associative mechanism.

Keywords: Kinetics, Mechanism, Substitution reaction, Organic bases

INTRODUCTION

The extensive studies on substitution reactions of amine complexes of cobalt(III) have mainly dealt with acid hydrolysis, base hydrolysis and substitution by anionic ligands in different solvents. The consensus on the mechanism is that the reactions involve a dissociative activation process [1-6].

There are, however, a few reports in the literature on systematic investigation of substitution by organic bases at cobalt(III) center [1]. Some of the qualitative studies with a methanolic solution of *trans*-$[Co(en)_2Cl_2]Cl$ have suggested that the reaction between organic bases and the complex showed a rate-dependence on the nature and concentration of the base. The observations have been explained on the basis of catalysis by methoxide ion and D_{cb} mechanism has been proposed [1]. However base hydrolysis studies on amine complexes of cobalt(III) which were examined by Tobe and coworkers showed that the mechanism followed is an associative (A) one [7-13].

In this work the rate of entry of five bases (diethylamine, triethylamine, benzylamine, t-butylamine and n-propylamine) into *trans*-$[Co(en)_2Cl_2]^+$ in DMA solution and I = 0.80 M $NaClO_4$ are studied spectrophotometrically and are explained on the basis of an associative mechanism.

EXPERIMENTAL

Preparation and Reagents

The complex *trans*-$[Co(en)_2Cl_2]Cl$ was prepared according to the literature [14], and converted to perchlorate by adding dilute perchloric acid to a dilute aqueous solution of the substrate [15]. The visible absorption spectra (λ_{max} = 618 nm, ε_{max} = 38 M^{-1} cm^{-1}) was in good agreement with the published spectra [16].

$CoCl_2.6H_2O$, ethylenediamine, H_2O_2, HCl and $NaClO_4$ were from Merck and Fluka. The bases were purchased from Merck and distilled before use. Analytical grade DMA from Merck was used without further purification.

Kinetic Studies

Substitution rates were determined spectrophotometrically at (30-55) ± 0.1 °C. In all cases, the procedure involved adding

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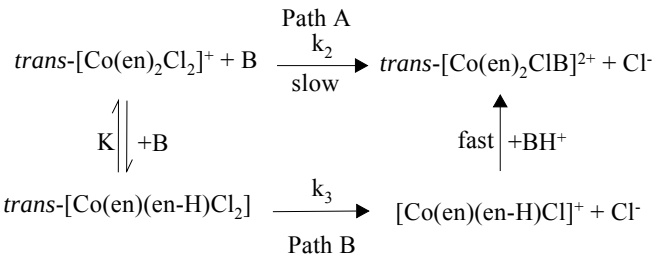
sample of a given base to a solution containing the substrate and enough perchlorate to maintain the ionic strength at 0.80 M. Light absorption measurements in the visible region were made using a PU 8750/Phillips spectrophotometer. The kinetics were followed at a predetermined wavelength (λ_{kin}), where the difference in absorbance between the substrate and the product was maximum. The products were prepared separately according to the literature [1] and their spectra in DMA were compared with the spectra of the reaction solution at equilibrium in each case (see Table 1). The temperature was thermostated at (30-55) ± 0.1 °C. 10-ml quartz cells were used. The k_{obs} values were calculated using a basic computer program (QB45) and the $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ values were evaluated by fitting the rate constants at various temperatures to Eyring equation (*i.e.*, $\ln(k_2/T)$ or $\ln(k_1/T)$ *vs.* 1/T) using the QPRO computer program. The rate constants were obtained at constant substrate concentration (0.005 M) and varying bases concentrations of bases (see Table 2).

RESULTS AND DISCUSSION

The rate constants for the entry of five organic bases into the *trans*-$[Co(en)_2Cl_2]^+$ in DMA solution at constant ionic strength of 0.80 M and various temperatures are listed in Tables 2. The data given in Table 2 were obtained from the slopes of the linear plots of k_{obs} *vs.* [B]. Samples of the resulting plots are shown in Figure 1. The rate laws (1) and (2) are compatible with Scheme 1.

$$k_{obs} = k_1 + k_2[B] \quad (1)$$

$$k_1 = k_3K[B]/(1 + K[B]) \quad (2)$$



Scheme 1

The reactions in Scheme 1 are followed by two distinct pathways to produce *trans*-$[Co(en)_2ClB]^{2+}$. Path (A) involves nucleophilic attack by a base to produce seven coordinated intermediate. Path B involves a unimolecular conjugate base mechanism, D_{cb}, leading to an intermediate species of five coordination number. Both paths are base-concentration dependent. However the span of k_2 values of path A in Table 2 shows that the direct base attack on the substrate is dependent upon the nature of the entering base, too.

For the conjugate base path B, the small differences in k_1 values (Table 2) indicate that it is base-concentration dependent but is not sensitive to the nature of the base (*i.e.*, less than 10 fold differences). The linear dependence of k_{obs} on [B] might imply that the concentration of any conjugate base formed is very small and proportional to [B]. The conjugate base path B under the condition where K [B]>> 1 implied that $k_1 = k_3$.

The stability of the substrate in DMA solvent was tested, and it was shown that the substitution of the chloride by DMA

Table 1. Spectrophotometric Data for Different Co(III) Complexes

Complex	λ_{max} (nm) (reaction solution)	λ_{max} (nm) (pure solution)	λ_{kin} (nm)
trans-$[Co(en)_2(diethylamine)Cl]^{2+}$	516	512	517
trans-$[Co(en)_2(triethylamine)Cl]^{2+}$	527	518	540
trans-$[Co(en)_2(benzylamine)Cl]^{2+}$	525	516	525
trans-$[Co(en)_2(t\text{-}butylamine)Cl]^{2+}$	518	511	518
trans-$[Co(en)_2(n\text{-}propylamine)Cl]^{2+}$	506	512	515

Table 2. Pseudo First-Order Rate Constants for the Reaction of *Trans*-$[Co(en)_2Cl_2]^+$ (0.005 M) with Different Bases (B) in DMA Solution at μ = 0.80 M and Various Temperatures

B = Diethylamine

	10^3 k_{obs} (s^{-1})						10^3 k_1 (s^{-1})	10^3 k_2 ($M^{-1}s^{-1}$)
B (M)	0.05	0.10	0.20	0.30	0.40	0.50		
30 °C	0.30(0.05)[a]	0.33(0.10)	0.37(0.02)	0.44(0.03)	0.48(0.03)	0.53(0.04)	0.28(0.00)	0.50(0.01)
35 °C	0.54(0.02)	0.59(0.03)	0.66(0.02)	0.74(0.04)	0.81(0.05)	0.88(0.09)	0.51(0.00)	0.75(0.01)
40 °C	0.69(0.02)	0.75(0.02)	0.81(0.07)	0.91(0.09)	1.02(0.06)	1.12(0.10)	0.64(0.01)	0.94(0.03)
45 °C	0.87(0.03)	0.92(0.01)	1.03(0.05)	1.13(0.09)	1.25(0.01)	1.40(0.16)	0.81(0.01)	1.14(0.04)
50 °C	1.16(0.08)	1.25(0.02)	1.39(0.18)	1.54(0.12)	1.66(0.15)	1.75(0.21)	1.12(0.02)	1.33(0.06)

B = Benzylamine

	10^3 k_{obs} (s^{-1})						10^3 k_1 (s^{-1})	10^3 k_2 ($M^{-1}s^{-1}$)
B (M)	0.05	0.10	0.20	0.30	0.40	0.50		
35 °C	0.90(0.05)	1.41(0.03)	2.26(0.05)	2.92(0.08)	3.55(0.33)	4.55(0.29)	0.60(0.08)	7.76(0.28)
40 °C	1.36(0.05)	2.13(0.11)	3.31(0.09)	4.29(0.12)	5.00(0.15)	5.91(0.07)	1.12(0.16)	9.86(0.55)
45 °C	2.99(0.05)	3.75(0.57)	4.78(0.46)	6.28(0.26)	7.12(0.45)	8.58(0.19)	2.45(0.12)	12.15(0.39)
50 °C	4.00(0.16)	4.53(0.28)	5.99(0.48)	7.55(0.30)	9.14(0.41)	10.48(0.41)	3.14(0.08)	14.73(0.26)

B = *t*-Butylamine

	10^3 k_{obs} (s^{-1})						10^3 k_1 (s^{-1})	10^3 k_2 ($M^{-1}s^{-1}$)
B (M)	0.10	0.20	0.25	0.30	0.35	0.40		
30 °C	0.95(0.07)	1.07(0.09)	1.14(0.11)	1.21(0.03)	1.27(0.01)	1.34(0.01)	0.81(0.01)	1.31(0.02)
35 °C	1.40(0.06)	1.57(0.21)	1.63(0.02)	1.70(0.02)	1.78(0.21)	1.86(0.02)	1.26(0.01)	1.50(0.03)
40 °C	2.64(0.16)	2.83(0.30)	2.92(0.22)	3.00(0.03)	3.08(0.17)	3.15(0.03)	2.47(0.01)	1.72(0.04)
45 °C	4.91(0.30)	5.08(0.27)	5.15(0.12)	5.30(0.10)	5.37(0.12)	5.53(0.35)	4.68(0.32)	2.03(0.11)

B = *n*-Propylamine

	10^3 k_{obs} (s^{-1})						10^3 k_1 (s^{-1})	10^3 k_2 ($M^{-1}s^{-1}$)
B (M)	0.05	0.10	0.15	0.20	0.25	0.30		
30 °C	2.08(0.04)	2.50(0.04)	2.98(0.05)	3.27(0.11)	3.68(0.07)	4.10(0.02)	1.71(0.04)	7.95(0.21)
35 °C	2.39(0.020	2.97(0.03)	3.57(0.06)	4.19(0.01)	4.73(0.02)	5.22(0.05)	1.84(0.04)	11.47(0.21)
40 °C	3.97(0.04)	4.82(0.06)	5.44(0.08)	6.52(0.02)	7.11(0.02)	8.18(0.04)	3.10(0.12)	16.59(0.61)
45 °C	5.62(0.08)	6.45(0.03)	7.97(0.03)	8.99(0.04)	10.47(0.26)	11.43(0.02)	4.28(0.16)	24.07(0.84)

Table 2. Continued

B = Triethylamine

	10^3 k_{obs} (s^{-1})							
B (M)	0.10	0.20	0.40	0.60	0.80	1.00	10^3 k_1 (s^{-1})	10^3 k_2 ($M^{-1}s^{-1}$)
35 °C	0.88(0.05)	1.00(0.06)	1.16(0.07)	1.32(0.11)	1.47(0.11)	1.71(0.04)	0.80(0.01)	0.87(0.03)
40°C	1.00(0.05)	1.10(0.06)	1.41(0.07)	1.67(0.11)	1.85(0.10)	2.05(0.13)	0.90(0.03)	1.19(0.05)
45 °C	1.57(0.06)	1.70(0.10)	2.05(0.16)	2.24(0.14)	2.51(0.11)	2.91(0.06)	1.42(0.04)	1.43(0.07)
50 °C	1.98(0.09)	2.12(0.06)	2.43(0.22)	2.90(0.10)	-	-	1.76(0.03)	1.84(0.10)
55 °C	2.43(0.17)	2.61(0.10)	3.07(0.08)	3.66(0.09)	-	-	2.16(0.04)	2.42(0.12)

[a] Values in parentheses are standard deviations of k_{obs}.

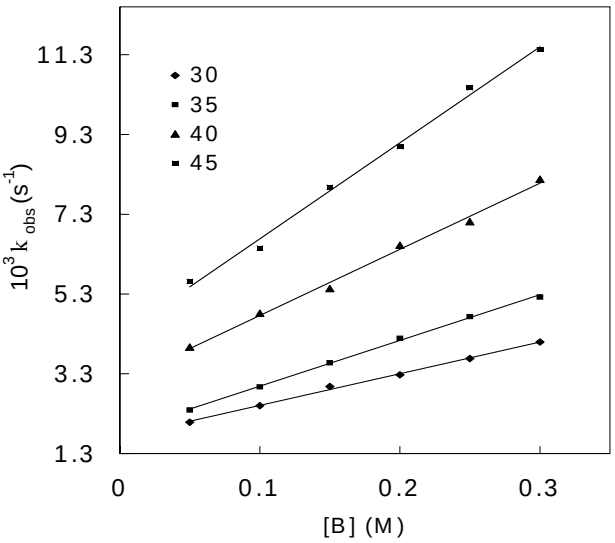


Fig. 1. The plots of k_{obs} *vs.* [*n*-propylamine] in DMA solution at μ = 0.80 M and different temperatures.

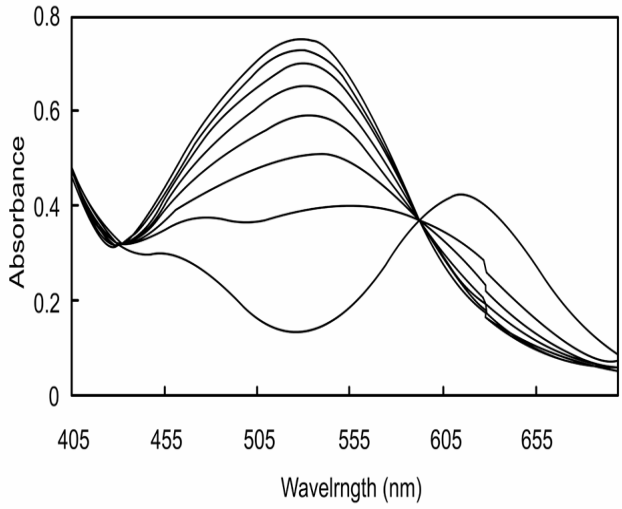


Fig. 2. Absorption spectra of *trans*-$[Co(en)_2Cl_2]^+$ -*n*-propylamine system in DMA at 40 °C.

was so slow that it did not interfere with the reaction of organic bases. Therefore, the two paths were proceeded without solvent intervention.

The absorption spectra of *trans*-$[Co(en)_2Cl_2]^+$ in the presence of various concentrations of the bases used were obtained, and sample spectra for *trans*-$[Co(en)_2Cl_2]^+$-*n*-propylamine system at 40 °C are shown in Fig. 2. As is obvious, the isosbestic points in Fig. 2 at 40 °C for the *n*-propylamine reaction were located at 435 and 595 nm, and for reactions of other bases were observed at 438 and 609 nm for triethylamine, 417 and 600 nm for benzylamine and 560 nm for *t*-butylamine.

The existence of such sharp isosbestic points indicated that the organic bases have substituted only one chloride ion in the substrate. The second chloride replacement is so slow that it does not interfere with the first chloride reaction. The reactions of the substrate with the given organic bases are

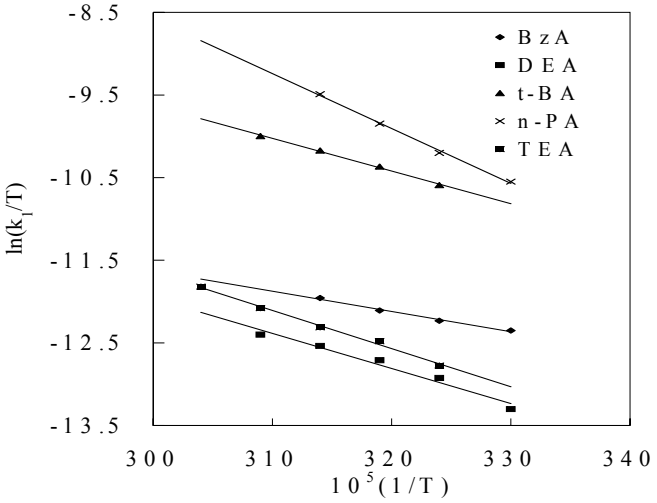


Fig. 3. Eyring plots of $\ln(k_1/T)$ *vs.* 1/T for the reaction of different bases with *trans*-$[Co(en)_2Cl_2]^+$ in DMA solution.

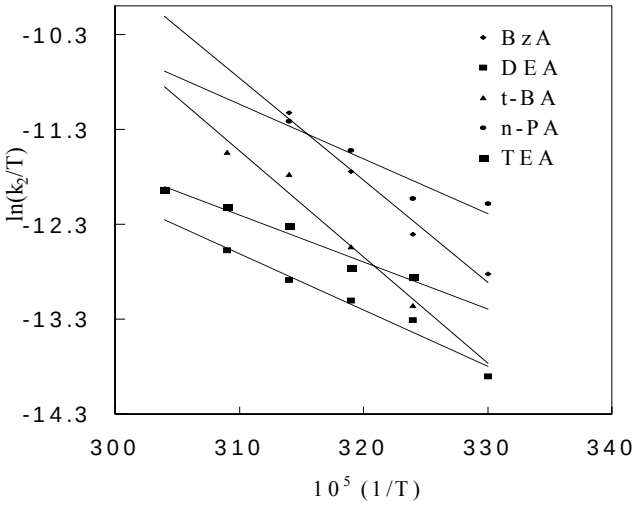


Fig. 4. Eyring plots of $\ln(k_2/T)$ *vs.* 1/T for the reaction of different bases with *trans*-$[Co(en)_2Cl_2]^+$ in DMA solution.

Table 3. Kinetic Activation Parameters for the Reaction *trans*-$[Co(en)_2Cl_2]^+$ + B ⟶ *trans*-$[Co(en)_2BCl]^{2+}$ + Cl^- in DMA Solution[a]

B	$\Delta H_1^{\ddagger}$ (kJ mol^{-1})	$\Delta H_2^{\ddagger}$ (kJ mol^{-1})	$\Delta S_1^{\ddagger}$ (J $K^{-1}mol^{-1}$)	$\Delta S_2^{\ddagger}$ (J $K^{-1}mol^{-1}$)	$\Delta G_1^{\ddagger}$[b] (J mol^{-1})	$\Delta G_2^{\ddagger}$[b] (J mol^{-1})	$10^3 k_1$[b] (s^{-1})	$10^3 k_2$[b] ($M^{-1} s^{-1}$)
Diethylamine	49.4(0.6)	35.3(3.5)	-149(2)	-191(11)	96(7)	95(5)	0.64(0.01)	0.94(0.03)
Triethylamine	41.3(4.5)	38.4(1.7)	-171(14)	-179(5)	95(6)	95(2)	0.90(0.03)	1.19(0.05)
Benzylamine	89.7(1.0)	20.3(1.4)	-9 (3)	-234(5)	93(9)	93(2)	2.48(0.01)	1.73(0.04)
t-Butylamine	93.2(1.5)	32.9(1.3)	-5(1)	-179(4)	95(13)	89(2)	1.12(0.16)	9.86(0.55)
n-Propylamine	48.0(11)	55.2(2.0)	-141(35)	-103(6)	92(16)	88(3)	3.14(0.12)	16.6(0.6)

[a] Values in parentheses are the standard deviations. [b] Values at 40 °C.

consistent with the trans chloro-base product and the spectroscopic evidence shows that there is no stereochemical rearrangement in the system (see Table 1). No evidence for any intermediate DMA complex was observed.

The activation parameters $\Delta S_2^{\ddagger}$, $\Delta S_1^{\ddagger}$, $\Delta H_2^{\ddagger}$, $\Delta H_1^{\ddagger}$ were evaluated from the corresponding standard linear Eyring plots of $\ln(k_2/T)$ and $\ln(k_1/T)$ *vs.* 1/T, with satisfactory correlation coefficients of 0.90 to 0.99. The resulting Eyring plots are shown in Figs. 3 and 4, and all calculated activation parameters are given in Table 3. As is obvious, both paths shown in Scheme 1 are $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ dependent.

The very large negative $\Delta S_2^{\ddagger}$ values given in Table 3 confirm that the associative mechanism for the direct path A is in operation. The lower negative $\Delta S_1^{\ddagger}$ values, especially for benzylamine and *t*-butylamine, show that some base assisted dissociative mechanism is predominated for path B. Moreover, the large span of $\Delta G_2^{\ddagger}$ (7 J mol^{-1}) compared with the lower span of $\Delta G_1^{\ddagger}$ (4 J mol^{-1}) signify the difference in mechanism for the two paths (see Table 3). Also the lower spans of $\Delta H_2^{\ddagger}$ (34.9 kJ mol^{-1}) and of $\Delta S_2^{\ddagger}$ (131 J K mol^{-1}), compared with $\Delta H_1^{\ddagger}$ (51.9 kJ mol^{-1}) and $\Delta S_1^{\ddagger}$ (162 J K mol^{-1}) confirm the associative operation of path A with respect to the dissociative

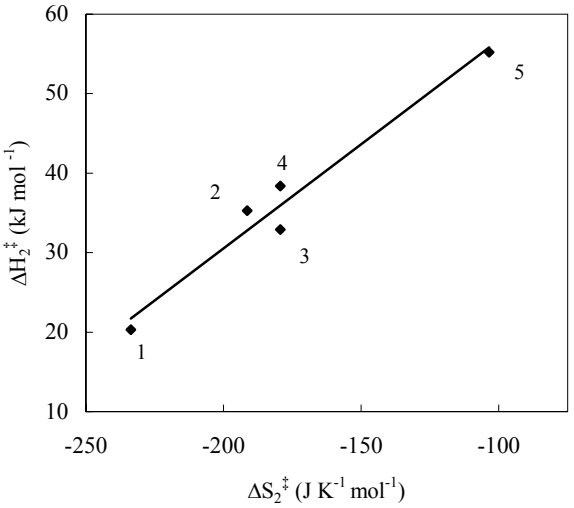


Fig. 5. Isokinetic plot for bimolecular reactions (path A) of *trans*-$[Co(en)_2Cl_2]^+$ with different organic bases in DMA solution: (1) benzylamine, (2) diethylamine, (3) triethylamine, (4) *t*-butylamine, (5) *n*- propylamine.

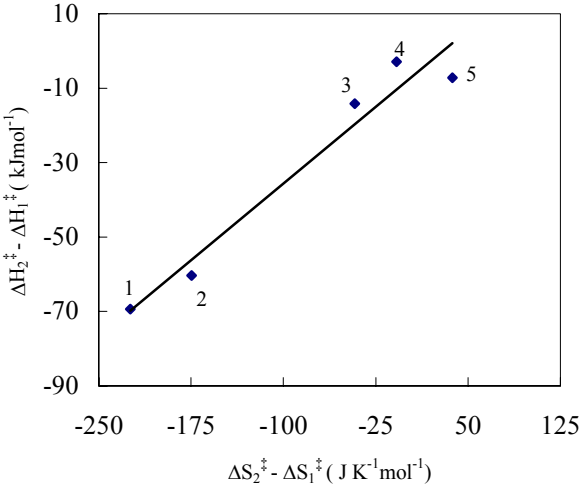


Fig. 6. Pseudo-isokinetic plot for the reaction of *trans*-$[Co(en)_2Cl_2]^+$ with different organic bases in DMA solution: (1) benzylamine, (2) *t*-butylamine, (3) diethylamine, (4) triethylamine, (5) *n*-propylamine.

conjugate base path B. The high negative values of $\Delta S_1^{\ddagger}$ show that the deprotonation in path B is the rate determining step, while the low negative values for benzylamine and *t*-butylamine show that the chloride departure from the complex conjugate intermediate is the rate determining step.

The isokinetic plot for the main path A (Fig. 5) with a correlation coefficient of 0.96 and a slope corresponding to an isokinetic temperature of -10.9 °C supports the fact that the bimolecular direct reactions follow the same associative mechanisms. However, no real isokinetic relationship for the path B is observed.

The very wide ranges of the activation enthalpy difference $\Delta H_2^{\ddagger}$ - $\Delta H_1^{\ddagger}$ of 69.4 kJ mol^{-1} and of the activation entropy difference $\Delta S_2^{\ddagger}$ - $\Delta S_1^{\ddagger}$ of -225 J K^{-1} mol^{-1} show that the mechanism is mainly of associative nature (see Table 3). Also, the linear pseudo-isokinetic plot in Fig. 6 with a correlation coefficient of 0.95 shows that all the systems studied in this work follow the same mechanism. The slope of the linear plot in Fig. 6, which corresponds to a pseudo-isokinetic temperature of 1.8 °C, shows that, at this temperature, the values k_2/k_1 are the same for all the reactions [17].

The nucleophilicity trend of the organic bases used towards the Co(III) substrate in path A, Scheme 1 is as follows: *n*-propylamine > *t*-butylamine > benzylamine > triethylamine > diethylamine (*i.e.*, with respective 10^3 k_2 of 16.6, 9.86, 1.73, 1.19 and 0.95 M^{-1} s^{-1}).

The reactivity order of the organic bases towards the Co(III) center is almost compatible with their steric effects rather than their basicity characters. When steric character increases, the tendency to Co(III) center will also decrease. Concerning this effect, the primary amines have more tendency to Co(III) center than the secondary and tertiary amines. However, because of the steric similarity of the secondary and tertiary amines, the tendency to the substrate is affected by basicity.

Triethylamine is a better base in organic solvents than other amines [18,19]. However, because of its B-strain, it does not form the base-product with the substrate easily.

As a result, the major factor in the reactivity of the organic bases for the replacement reactions firstly is governed by the steric and secondly by the basicity factor.

For primary amines, since the steric factors are almost similar, the basicity factor can determine which amine has more tendency to the Co(III) center. *n*-Propylamine and *t*-

butylamine have base strengths more than benzylamine [18,19]. Therefore, their tendency to Co(III) center is more than benzylamine. The basicity characters of *n*-propylamine ($K_b = 4.1 \times 10^{-4}$ in water) and *t*-butylamine ($K_b = 5.0 \times 10^{-4}$ in water) are almost similar; therefore, less steric *n*-propylamine has more tendency to the Co(III) center [13]. However, the basicity strengths of organic bases are determined by the competing factors such as steric, induction and solvation [20].

In an associative mechanism, the rate is very sensitive to the nature of the entering group. It is usual to use the term nucleophilicity as a quantitative measure of reactivity of the entering group. Many years ago, Swian and Scott [21] set up a quantitative scale for tetrahedral carbon and interest in the relationship between the factors controlling nucleophilicity such as basicity and steric factors and the nature of the reaction center was one of the features that led Pearson [22] to develop the concept of hard and soft acids and bases.

In general, the factors that promote nucleophilicity at Co(III) are those that are associated with class (a) or hard behavior, which is not surprising in view of the fact that the reaction center is also typically class (a) or hard. This is characterized by the micropolarizability of the donor rather than its proton basicity.

The observed trend in bases used in this work show that amines are in general hard species, but electron donation of the groups attached to the nitrogen atom changes its hardness property. Therefore, the strength of interaction of any base with the Co(III) center is determined by its k_2 value, which signifies that, despite its lower basicity character ($K_b = 4.1 \times 10^{-4}$), *n*-propylamine, is the hardest among the series studied ($k_2 = 16.6 \times 10^{-3}$ M^{-1} s^{-1}). Such comparisons require care; seldom is one factor totally responsible for the reaction, and the reaction is almost always a competition between acid-base or donor-acceptor pairs. For this reason, any predictions based on HSAB must be considered tentative.

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