[Contribution from the Department of Chemistry, University of Minnesota]

The *cis–trans* Isomerization of Dichlorobis-(ethylenediamine)-cobalt(III) Chloride and Dichlorobis-(propylenediamine)-cobalt(III) Chloride in Alcohols[1]

By Robert C. Brasted and Chikara Hirayama

Received August 7, 1957

The rates of isomerization of *cis*-dichlorobis-(propylenediamine)-cobalt(III) chloride and *cis*-dichlorobis-(ethylenediamine)-cobalt(III) chloride in alcoholic solution are of first order with respect to the complex, and zero order with respect to added chloride and perchlorate ions. The rates of the reaction in each solvent (methanol, ethanol and propanol) have frequency factors of 10^{12} to 10^{13} sec.$^{-1}$, and small positive entropies of activation. It is suggested that the isomerization is unimolecular and that the activated complex closely resembles the initial state of the reactant. It is proposed that pentacoördinated intermediate exists as a result of the approach of a perchlorate ion *trans* to the *cis*-coördinated chlorides ultimately resulting in a *trans* configuration of the dichloro complex. The dependence of the rates in the different solvents is attributed partially to ion-pair effect as indicated by studies in the presence of traces of moisture.

Historical Background

The mechanism and kinetic studies on the isomerization of cobalt(III) chloro complexes is complicated in aqueous systems because of the competition between the chloride ion and water for the cobalt ion. The present investigation has utilized alcoholic media for such studies.

Werner and McCutcheon[2] treated *l-cis*-dichlorobis-(ethylenediamine)-cobalt(III) ion with an aqueous solution of potassium carbonate and obtained the *l*-carbonatobis-(ethylenediamine)-cobalt(III) complex. When the aqueous solution of the *l-cis*-dichloro complex is allowed to stand before adding the silver carbonate, the *d*-carbonato complex results.[3] The results of Bailar and co-workers[3] suggest an intermediate aquation step in going from the *l*- to *d*-substitution product. The mechanism of this step becomes clearer when the work of Mathieu[4] is considered. It was shown that optically active $[Co(en)_2Cl_2]Cl$ undergoes mutarotation to $[Co(en)_2(H_2O)Cl]Cl_2$ at a similar rate to that of chloride ion formation. In addition, Mathieu has shown that the aquo-complex appears to have the same configuration as the original dichloro complex.

Bailar and co-workers[5] also converted the *l-cis*-dichlorobis-(ethylenediamine)-cobalt(III) chloride in liquid ammonia into the *cis*-diammine ion with either the *d* or *l*-form in excess, depending upon the temperature. The conversion obviously involves steps in which there are changes in configuration, although the work of these authors does not clearly define the changes.

Jorgensen[6] first observed the *cis–trans* isomerization of dichlorobis-(ethylenediamine)-cobalt(III) complex. Drew and Pratt[7] suggested a mechanism for this process which was later disproved by Ettle and Johnson.[8] However, there was an agreement in postulating a bimolecular mechanism. Brown, Ingold and Nyholm,[9,10] in the course of studying the stereochemistry of octahedral substitution, have proven that the *cis–trans* isomerization of dichlorobis-(ethylenediamine)-cobalt(III) ion takes place by a monomolecular mechanism, eliminating the bimolecular mechanism of Ettle and Johnson.

The mechanism is described by Brown and Nyholm[9]

$$cis\text{-}[Co(en)_2Cl_2]^+ \underset{\text{fast}}{\overset{\text{slow}}{\rightleftarrows}} [Co(en)_2Cl]^+ + Cl^- \xrightarrow[\text{fast}]{X^-} trans\text{-}[Co(en)_2ClX]^+ \quad (I)$$

where X^- is nitrate, halide or thiocyanate ion. These reactions are independent of the substituting anions X^-, and result in complete loss of optical activity. The reaction has a positive ionic strength effect which is of the same order of magnitude as some of the ionic strength effects associated with the unimolecular substitutions of alkyl halides in hydroxylic solvents.[11] The rate of isomerization at 35.8° was increased by a factor of only 1.5 with a 50-fold increase in chloride concentration. The reaction also showed a retarding mass effect. This effect has been shown to be a unique characteristic of a unimolecular mechanism.[11] These investigators employed methanol solutions to study the substitution of weakly nucleophilic ligands to minimize the solvolytic effect since water readily replaces coördinately bound chloride, nitrate and thiocyanate from their complexes. Brown and Ingold[10] have shown that there is no solvolysis of any kind in the mechanism since there was no net chloride liberated when radioactive chloride was employed.

Brown and Nyholm[9] find that there is a larger energy barrier resisting the entry of chloride ion into the cobaltium ion to form the *trans*- than that in forming the *cis*-dichloro isomer. From these considerations they have concluded that the initial step in the isomerization is the heterolysis yielding a trigonal bipyramid cobaltium ion

(II)

The initial formation of the trigonal bipyramidal cobaltium ion is in agreement with the observations of Mathieu.[3] More recently, Pearson and

---

[1] In part from the Thesis of Chikara Hirayama, presented in partial fulfillment for the Ph.D., University of Minnesota, Minneapolis, Minnesota.

[2] A. Werner and M. McCutcheon, *Ber.*, **45**, 3291 (1912).

[3] J. C. Bailar, Jr., and D. F. Peppard, *ibid.*, **62**, 820 (1940).

[4] J. P. Mathieu, *Bull. soc. chim.*, **3**, 476, 2121 (1936).

[5] J. C. Bailar, Jr., J. H. Haslam and E. V. Jones, This Journal, **58**, 2226 (1936).

[6] S. M. Jorgensen, *J. prakt. Chem.*, **39**, 16 (1889); **41**, 449 (1890).

[7] H. D. K. Drew and N. H. Pratt, *J. Chem. Soc.*, 506 (1937).

[8] G. W. Ettle and C. H. Johnson, *ibid.*, 1490 (1939).

[9] D. D. Brown and R. S. Nyholm, *ibid.*, 2696 (1953).

[10] (a) D. D. Brown, C. K. Ingold and R. S. Nyholm, *ibid.*, 2674 (1953); (b) D. D. Brown and C. K. Ingold, *ibid.*, 2680 (1953).

[11] L. G. Bateman, M. C. Church, E. D. Hughes, C. K. Ingold and N. A. Taher, *ibid.*, 979 (1940).

Basolo[12] considered the configuration of the pentacovalent intermediate from bond orbital considerations, and have shown that the trigonal bipyramidal configuration is the most plausible. These latter authors have shown that the stereochemistry of practically all *cis–trans* isomers concerned will take place in agreement with this configuration.

Werner and Frohlich[13] first prepared dichlorobis-(propylenediamine)-cobalt(III) complexes and found these compounds to have very similar properties to the corresponding ethylenediamine complexes. For example, there is a remarkable spectrophotometric similarity between the corresponding complexes of ethylenediamine and propylenediamine. However, because of the methyl group substituted on a carbon atom of ethylenediamine, the propylenediamine complex has a more complicated system stereochemically than that of ethylenediamine. Regardless of the stereochemical complication it would seem that the isomerization of *cis*-dichloro to *trans* complex should take place by a monomolecular mechanism.

Pearson and co-workers[14] have studied the acid hydrolysis of complexes of the type *trans*-$[Co(AA)_2Cl_2]^+$, where AA was varied from the comparatively simple ethylenediamine to the more complicated substituted amino ligands. It was found in this study that the acid hydrolysis was of first order in every case. The rate of hydrolysis increased as the complexity of the ligand increased such that there was an increased crowding around the central ion. These authors claim that the increasing rate with complexity of the ligand is compatible with the S_N1 mechanism in which a pentacovalent intermediate is formed. Thus dichlorobis-(propylenediamine)-cobalt(III) ion was found to hydrolyze at a greater rate than the corresponding ethylenediamine complex.

In the present study some preliminary experiments proved that the rate of isomerization of *cis*-dichlorobis-(propylenediamine)-cobalt(III) chloride in methanol proceeds at a slower rate than the corresponding ethylenediamine complex. The effect of added salts on the rate of the reaction of the propylenediamine complex was that of retarding the reaction. It was therefore proposed to study the isomerization of *cis*-dichlorobis-(ethylenediamine)-cobalt(III) chloride and *cis*-dichlorobis-(propylenediamine)-cobalt(III) chloride with respect to the effect of common ion and perchlorate ion on the rate of the reaction, and also to study the effect of different solvents on the rates of isomerization.

Kinetics of Monomolecular Complex Reactions

For a monomolecular reaction of an ion A^n

$$A^n \rightleftarrows X^n \longrightarrow B \qquad \text{(III)}$$

where X^n is the transition state complex, we have the rate expression

$$v = kc_A(f_A/f_X) \qquad \text{(IV)}$$

where f_A and f_X are the activity coefficients of the reactant and transition state complex, respectively, v is the rate of the reaction, k is the rate constant and c_A is the concentration of the reactant. The charge on the transition state complex is generally assumed to be the sum of the charges on the reactants. La Mer[15] earlier indicated that the activity coefficient of the transition state complex is in general not identical to that of the reactant. Knox and Trotman-Dickenson[16] have noted discrepancies in the calculated frequency factors for some reactions caused by erroneous assumptions in the configurations of the activated complex.

Ingold and co-workers[11] have treated the salt effect of monomolecular reactions involving the solvolysis of alkyl halides. The rate relationship derived for these reactions was based on the effect of ionic strength on a dipolar, (R–X), molecule in which the activated complex is also a dipole. The results of this treatment were used by Brown and Ingold[10] in their interpretation of the monomolecular mechanism involving substitution in octahedral inorganic complex ions. Their conclusion was that a monomolecular reaction had a positive salt effect and a negative mass effect.

In the case of a monomolecular reaction involving ionic reactants, the system becomes simpler than that for a dipolar reactant. If it is assumed that the activity coefficient of the activated complex differs much more from unity than that of the unactivated complex, the rate expression is expressed by

$$v = kc_A/f_X \qquad \text{(V)}$$

If as stated by La Mer,[15] the molecular field surrounding the activated complex is much different from that around the unactivated complex, our assumption will be justified. The relationship between k in equation V and the measured first-order rate constant k_1 is

$$k_1/k = 1/f_X \qquad \text{(VI)}$$

Using the logarithm of equation VI and substituting the Debye–Hückel relationship for $\log f_X$, the expression

$$\log k_1 = \log k + [e^2Z^2/2.303(2DkT)]K/(1 + Ka) \qquad \text{(VII)}$$

is derived, in which e is the electronic charge, Z is the charge on the ion, k is Boltzmann's constant, a is the ionic diameter, T the temperature, and K is defined by

$$K = 15.2 \times 10^8 \mu^{1/2}/DT \qquad \text{(VIII)}$$

D is the dielectric strength and μ the ionic strength of the solution in equation VIII.

Equation VII shows that the rate of a monomolecular reaction involving ions increases with increasing ionic strength. In accordance with Ingold and co-workers,[11] we would also expect a decreasing mass effect.

It is seen that the rate of a monomolecular reaction at zero ionic strength should be identical in all solvents. In a bimolecular reaction there is a definite relationship between the rate at infinite dilution and the dielectric constant of the solvent.[17] Moel-

---

[12] R. G. Pearson and F. Basolo, THIS JOURNAL, **78**, 4878 (1956).

[13] A. Werner and A. Frohlich, *Ber.*, **40**, 2225 (1907).

[14] R. G. Pearson, G. R. Boston and F. Basolo, THIS JOURNAL, **75**, 3089 (1953).

[15] V. K. La Mer, *Chem. Revs.*, **10**, 179 (1932).

[16] J. H. Knox and A. F. Trotman-Dickenson, *J. Phys. Chem.*, **60**, 1367 (1956).

[17] S. Glasstone, K. J. Laidler and H. Eyring, "The Theory of Rate Processes," McGraw-Hill Book Co., New York, N. Y., 1941, p. 430.

wyn-Hughes[18] states, however, that the general effect of changing the solvent is to bring about a change in both E_A and A in the Arrhenius equation. Both changes are in the same direction. In the case of bimolecular reactions involving two ions, or an ion and a dipolar molecule, we would not necessarily expect to find the rates the same in two solvents of comparable dielectric constant since the ionic diameters vary from solvent to solvent.

If the mechanism involves a bimolecular collision between a charged ion and a solvent molecule, there should be no salt effect in dilute solutions. However, at high ionic strengths the rate constant increases linearly with the ionic strength.[19]

Experimental

Preparation of Compounds and Solutions.—*cis*-Dichlorobis-(ethylenediamine)-cobalt(III) chloride (I) and *cis*-dichlorobis-(propylenediamine)-cobalt(III) chloride (II), were prepared by already described methods.[20] The methanol, ethanol and propanol were dried with sodium and redistilled, the middle fractions being used for making the solutions.

Preparation of Salt Solutions.—The salts used were of reagent grade. Lithium chloride and sodium perchlorate were heated at 250 to 275° for at least two days before being used. Sodium chloride was ground and heated to red heat. The solutions of these salts in the alcohols were made by pouring the hot salt into glass-stoppered volumetric flasks which contained the alcohol. Sodium chloride dissolves to an appreciable extent only in methanol. The salt solutions were made just before they were used. Solutions approximately 0.001 M were made by pipetting one and five ml. of a freshly made concentrated solution (about 0.1–0.15 M), and transferring into a dry 250-ml. flask. The solution was then diluted to the mark in a nitrogen atmosphere.

Preparation of Solutions of Complex Ions.—Solutions of complexes I and II in methanol were made by dissolving weighed quantities in a volumetric flask. The solution of the complexes in ethanol and propanol were made by shaking the solid complex with the solvent in 100-ml. glass-stoppered flasks for not more than five minutes in a nitrogen atmosphere, then decanting into a dry flask, or into the absorption flask for measurement. The concentration of the complex was then calculated from the absorption coefficient and initial absorbance of the solution in the respective solvents. This method is accurate to within 2 or 3% since the rate of isomerization in ethanol and propanol for both complexes is quite slow, such that the absorbance does not decrease by more than 0.001 division in five to ten minutes at room temperature. Solutions of the complexes in the alcoholic salt solutions were made in similar manner on the freshly prepared salt solutions. The solutions for the 25° measurement were made by first placing the alcohol in the thermostat bath at 25°.

Kinetic Measurements.—The rates were measured on a Beckman Model DU spectrophotometer at a wave length of 540 mμ. One centimeter fused quartz cells with matched ground glass stoppers were used. The cell compartment of the spectrophotometer was jacketed for water circulation, and was thermostated by pumping water through the jacket. The temperature in the cell compartment was controlled to within ±0.1°.

The measurements at 25° were made by placing the stoppered cell containing the solution in the cell compartment of the spectrophotometer, and making the initial absorbance reading within ten minutes after the solution of the complex was prepared in each case. The initial reading was taken as zero time. There is a small uncertainty in this zero time since the temperature of the solution was usually slightly lower than 25° when the cell was placed in the spectrophotometer, and the time required to attain temperature equilibrium was estimated to be at least ten minutes. The effect of the 540 mμ light band on the complex solution under the experimental conditions was found to be negligible, although the effect of sunlight on the rate was very marked.

The absorbance reading at infinite time was obtained in two ways: (1) the reaction was allowed to go to completion; (2) the final absorbance reading was calculated from the known absorption coefficient of the *trans* complex and the concentration of the solution. The second method was found to be valid throughout for complex (I). The second method was also in general agreement with complex (II) but due to a slight uncertainty in the absorption coefficient at the *trans* isomer in the alcohols the reactions of this complex were carried out to completion in nearly all runs. Kinetic measurements were made on duplicate runs, excepting the salt effects at 25°, to at least two half-lives.

The measurements in methanol at 30, 35 and 40° were made by dissolving the complex rapidly at around 15° in darkened flasks, which were subsequently placed in the kerosene bath controlled to within ±0.02°. The initial sample was transferred to the absorption cell and the reading made within a minute. Zero time was taken as two minutes after the flask was placed in the bath. Samples were withdrawn at different time intervals with a dry pipet which had been flushed with dry nitrogen. A stream of nitrogen was passed into the flask as the sample was withdrawn. Brown and Ingold[9] estimated that the methanol solutions absorbed about 0.01 to 0.1% of water during the preparation of their solutions. The effect of this amount of moisture on the rate in pure methanol solutions was found to be negligible under the conditions studied. However, the rates of isomerization in ethanol and propanol solutions were highly sensitive to small amounts of water.

The rate studies in ethanol and propanol at 30 to 40° were carried out in specially constructed flasks which utilized a siphon system. The solutions were made in a nitrogen atmosphere at room temperature, and transferred to the blackened flask of the siphon system under nitrogen. Air was excluded at all times. The initial reading was made within 10 minutes after the solution was made by siphoning a sample into the absorption cell by using nitrogen pressure. After the initial reading was made, the flask was placed in the thermostat and the initial time recorded after two minutes. Samples were withdrawn at different time intervals by siphoning under nitrogen pressure.

The effect of lithium chloride on the rate of isomerization of complex II was studied in ethanol and propanol solutions. The effect of sodium perchlorate in ethanol was also studied, but such an effect was not possible in propanol due to precipitation of the *trans* isomer in the presence of perchlorate ion.

The stoichiometry of the isomerization is simply represented by

$$cis\text{-complex} \longrightarrow trans\text{-complex}$$

That the transformation in all three alcohols is complete or very nearly so was confirmed by the absorption spectra of the initial and final solutions. The *cis*- and *trans*-complexes obey Beer's law in every case.

The rate constants were calculated by the integration method. Duplicate results agreed to within 10% and in most cases agreement was within 5%. The rate constants and thermodynamic data are recorded in Tables I and II.

Results

The rate of isomerization of *cis*-dichlorobis-(ethylenediamine)-cobalt(III) chloride in methanol was found to be in good agreement with those reported by Brown and Nyholm.[9] These authors report an energy of activation of 23.69 kcal. and a frequency factor of 5.09×10^{12} sec.$^{-1}$.

Sodium chloride was found to increase the rate of isomerization in methanol solutions at 25°. Brown and Nyholm[9] determined the effect of LiCl on the rate in methanol at 35.8°. They report an increase in rate of 1.5 times over that in the absence of LiCl when the ratio of chloride to complex was 52.3. Table III shows the results of the present investigation. The rate is at a maximum of 1.4 times the rate in the absence of chloride when the ratio of chloride to complex is 69. The rate then

---

[18] E. A. Moelwyn-Hughes, "The Kinetics of Reaction in Solutions," Oxford Press, 1947, p. 210.

[19] Ref. 17, p. 442.

[20] H. Biltz and W. Biltz, "Laboratory Methods of Inorganic Chemistry," translated by W. T. Hall and A. A. Blanchard, John Wiley and Sons, Inc., New York, N. Y., 1909.

TABLE I

RATES OF ISOMERIZATION OF *cis*-$[Co(en)_2Cl_2]Cl$ AND *cis*-$[Co(pn)_2Cl_2]Cl$ IN ALCOHOLS ($k \times 10^4$ min.$^{-1}$)

Temp., °C.	*cis*-$[Co(en)_2Cl_2]Cl$ Methanol	Ethanol	*cis*-$[Co(pn)_2Cl_2]Cl$ Methanol	Ethanol	Propanol
25.00	13.4 ± 0.6	10.4 ± 0.7	14.3 ± 0.4	6.0 ± 0.4	....
30.00	24 ± 2	19 ± 1	27 ± 1	15 ± 1	8.9 ± 0.6
35.06	44 ± 3	....	59 ± 2	25 ± 1	16 ± 2
40.05	84.5 ± 2	67 ± 3	100 ± 3	47 ± 2	34 ± 2

TABLE II

	cis-$[Co(en)_2Cl_2]Cl$		*cis*-$[Co(pn)_2Cl_2]Cl$		
	Methanol	Ethanol	Methanol	Ethanol	Propanol
E (kcal.)	23.4	23.5	23.9	24.5	25.2
A (sec.$^{-1}$ × 10^{12})	3.04	2.98	8.37	10.5	16.2
$\Delta S^{\ddagger}$ (e.u.)	3.5	3.4	5.4	5.9	6.8
$\Delta H^{\ddagger}_{298.16}$° K.(kcal.)	22.8	22.9	23.3	23.9	24.6
$\Delta F^{\ddagger}_{298.16}$° K.(kcal.)	21.8	21.9	21.7	22.1	22.6

drops to 1.25 times the rate in pure solvent as the concentration of chloride increases. A mass effect was observed similar to that reported by Brown and Ingold.[10c]

TABLE III

EFFECT OF NaCl ON RATE OF ISOMERIZATION OF *cis*-$[Co(en)_2Cl_2]Cl$ IN METHANOL AT 25.00°

[NaCl] mole/l.	0.172	0.132	0.0058	0.0023	0.058
$[Coen_2Cl_2]Cl \times 10^{-3}$ mole/l.	.58	.80	.80	.79	.84
μ	.173	.133	.0066	.0031	.059
$k \times 10^{-3}$ min.$^{-1}$	1.66	1.69	1.46	1.40	1.91
$[Cl^-]/[Coen_2Cl_2]^+$	279	265	7.3	2.9	69

The rate of isomerization of *cis*-dichlorobis-(ethylenediamine)-cobalt(III) chloride in ethanol was found to be 0.78 times that in methanol at 25.00°. Due to the low solubility of the complex in ethanol, the accuracy of the rate constants in this solvent was the lowest of all the determinations. The average percentage error on the standard deviation was 7%. Nevertheless, the rate in ethanol was significantly lower than that in methanol. The rate varied linearly with the temperature. The frequency factor and energy characteristics in ethanol were nearly identical with the reaction in methanol.

The *cis*-dichlorobis-(propylenediamine)-cobalt(III) chloride isomerizes at a slightly faster rate in methanol than the analogous ethylenediamine complex. The temperature coefficient of the rate was slightly higher in the former, and this increase is manifested in the higher value of 8.37 × 10^{12} for the frequency factor.

The effect of chloride and perchlorate on the rate of isomerization was studied at 25.00 and at 35.06°. The salt effect at the lower temperature was studied to compare the results with those obtained for the same temperature of *cis*-$[Co(en)_2Cl_2]Cl$. The study at the higher temperature was made to compare the results against those of Brown and Nyholm[9] for the ethylenediamine complex. The results of the effect of chloride on the rate are summarized in Table IV.

A very significant factor with respect to the effect of salts on the isomerization rate of *cis*-dichlorobis-(propylenediamine)-cobalt(III) is that the rate of isomerization is decreased by the presence of salts. This effect, although small, is opposite to that obtained for *cis*-dichlorobis-(ethylenediamine)-cobalt(III) chloride in salt–methanol solutions. At 25.00° the ratio of the rate in the absence of salt to that in its presence is 1.34 when the ratio of sodium chloride to the complex is 18.5. The same rate was obtained when the latter ratio is 27. In the case of LiCl in methanol the rate was 1.29 times greater than that in the absence of the salt when the ratio of LiCl to complex was 21.8. The ratio of the rate in the absence of salt to that in the presence of LiCl was increased to 53.5. It is seen from Table IV that the effect of salt on the rate is non-linear.

TABLE IV

EFFECT OF NaCl AND LiCl ON THE RATE OF ISOMERIZATION OF *cis*-$[Co(pn)_2Cl_2]Cl$ IN METHANOL

		35.06°			
[NaCl] mole/l.	0.177	0.1825	0.0413	0.0165	0.0088
$[Co(pn)_2Cl_2]Cl$ mole/l. × 10^{-3}	3.2	3.2	3.2	3.2	3.2
μ	0.180	0.086	0.044	0.020	0.0091
$k \times 10^{-3}$ min.$^{-1}$	5.07	5.36	5.72	6.04	6.10
$[Cl^-]/[Co(pn)_2Cl_2]^+$	55	25.8	12.9	5.2	2.7
		25.00°			
[NaCl] mole/l.	0.1071	0.0749	0.0529	0.0214	
$[Co(pn)_2Cl_2]Cl$ mole/l. × 10^{-3}	4.0	4.0	4.6	3.8	
μ	0.111	0.079	0.058	0.024	
$k \times 10^{-3}$ min.$^{-1}$	1.07	1.06	1.16	1.27	
$[Cl^-]/[Co(pn)_2Cl_2]^+$	27	18.5	11.5	5.6	
		35.06°			
[LiCl] mole/l.	0.0299	0.0816	0.205		
$[Co(pn)_2Cl_2]Cl$ mole/l. × 10^{-3}	3.1	3.1	3.2		
μ	0.033	0.085	0.208		
$k \times 10^{-2}$ min.$^{-1}$	5.77	5.68	5.82		
$[Cl^-]/[Co(pn)_2Cl_2]^+$	9.6	26.4	64		
		25.00°			
[LiCl] mole/l.	0.2194	0.110	0.0875		
$[Co(pn)_2Cl_2]Cl$ mole/l. × 10^{-3}	4.1	4.2	4.0		
μ	0.223	0.114	0.092		
$k \times 10^{-3}$ min.$^{-1}$	1.02	1.06	1.11		
$[Cl^-]/[Co(pn)_2Cl_2]^+$	53.5	26.2	21.8		

Typical results of salt effects are given in Table V.

The chloride salts have a definite mass effect, whereas, at high perchlorate concentrations, the rate increases as the reaction proceeds.

The effect of sodium chloride on the rate of isomerization of *cis*-dichlorobis-(propylenediamine)-cobalt(III) chloride at 35.06° is decreased from that at 25.00°. With a ratio of $[NaCl]/[Co(pn)_2Cl_2]^+$ of 5.2 there is no salt effect on the rate. When the ratio of salt to complex increases to 55 the rate increases to a ratio of 51/59.

Lithium chloride also decreases the rate of isomerization of the propylenediamine complex at 35.06°. Due to the large effect of traces of water

TABLE V

EFFECT OF $NaClO_4$ ON RATE OF ISOMERIZATION OF *cis*-$[Co(pn)_2Cl_2]Cl$ IN METHANOL AT 35.06°

Time, min.	log I_0/I	$n(r_0 - r_\infty)/(r_i - r_\infty)$	$k \times 10^3$
$[NaClO_4] = 0.209$, $[Co(pn)_2Cl_2]^+ = 3.22 \times 10^3$, $\mu = 0.212$			
0	0.207	0	..
38	.195	.0760	2.00
107	.161	.2394	3.08
196	.119	.7435	3.79
279	.095	1.149	4.12
345	.0805	1.476	4.28
413	.069	1.842	4.46
607	.0535	2.749	4.53
∞	.043	...	..
$[NaClO_4] = 0.02$, $[Co(pn)_2Cl_2]^+ = 3.2 \times 10^{-3}$, $\mu = 0.023$			
0	0.213	0	..
40	.183	0.1798	4.50
68	.164	.3134	4.61
94	.1415	.4990	5.31
127	.122	.6933	5.46
180	.098	.9993	5.55
210	.088	1.161	5.52
502	.043	2.720	5.42
∞	.031	...	..

EFFECT OF NaCl ON RATE OF ISOMERIZATION OF *cis*-$[Co(pn)_2Cl_2]Cl$ IN METHANOL AT 35.06°

Time, min.	log I_0/I	$n(r_0 - r_\infty)/(r_i - r_\infty)$	$k \times 10^3$
$[NaCl] = 0.177$, $[Co(pn)_2Cl_2]Cl = 3.2 \times 10^{-3}$, $\mu = 0.180$			
0	0.217	0	..
32	.190	0.1655	5.17
71	.1615	.3764	5.50
114	.138	.5912	5.19
155	.119	.8071	5.21
197	.1045	1.010	5.13
272	.0855	1.359	5.00
693	.049	2.980	4.30
∞	.040	Av.	5.05
$[NaCl] = 0.0165$, $[Co(pn)_2Cl_2]^+ = 3.2 \times 10^{-3}$, $\mu = 0.020$			
0	0.216	0	..
32	.1855	0.1816	5.68
69.5	.1525	.4247	6.11
99.5	.132	.6120	6.15
132	.114	.8120	6.15
198	.087	1.214	6.13
231	.077	1.417	6.13
371	.0525	2.217	5.98
689	.0365	3.827	5.55
∞	.0325	Av.	5.98

EFFECT OF LiCl ON RATE OF ISOMERIZATION OF *cis*-$[Co(pn)_2Cl_2]Cl$ IN METHANOL AT 35.06°

Time, min.	log I_0/I	$n(r_0 - r_\infty)/(r_i - r_\infty)$	$k \times 10^3$
$[LiCl] = 0.0816$, $[Co(pn)_2Cl_2]^+ = 3.1 \times 10^{-3}$, $\mu = 0.085$			
0	0.2075	0	..
50.5	.167	0.2769	5.48
88	.141	.5057	5.75
128	.1205	.7330	5.75
169	.1035	.9702	5.74
∞	.040	Av.	5.68

on the rate, the results obtained are not as dependable as desired at this temperature. At 25° the effect of water in lithium chloride solutions was small due to the lower rate of isomerization, as compared to 35.06°, and to the manner of handling the samples for measurements. The effect of water was minimized by the exclusion of air in handling the samples.

The effect of sodium perchlorate on the rate of isomerization of the propylenediamine complex is different from that of sodium and lithium chlorides. The rate in the former salt solutions is unaffected by traces (0.05%) of water. In the sodium perchlorate systems the initial rates are about one-half of the initial rates in sodium chloride solutions of comparable concentrations. Whereas the rate decreased in the chloride salt solutions as the reaction progressed the rate increased in the perchlorate solutions. At a concentration of 0.209 *M* in perchlorate at 35.06°, the initial rate was 2.00×10^{-3} $min.^{-1}$. The rate progressively increased until it reached a value approximately 44×10^{-3} $min.^{-1}$ at about 80% completion. As the perchlorate concentration decreased, the initial rate increased and the system attained a constant rate earlier in the transformation. For example, at a perchlorate concentration of 0.023 *M* the average initial rate was 4.7×10^{-3} $min.^{-1}$, and a constant rate of 5.5×10^{-3} $min.^{-1}$ was attained when the reaction was approximately 50% complete.

The rate of isomerization of *cis*-dichlorobis-(propylenediamine)-cobalt(III) chloride was found to be lower than that for the ethylenediamine complex in the same solvent (see Table I). The rate of isomerization for the former complex was lowest in propanol solutions. There is a greater scattering of rates of *cis*-$[Co(pn)_2Cl_2]Cl$ in ethanol and propanol than for the other systems. The rates of isomerization of *cis*-$[Co(pn)_2Cl_2]Cl$ in ethanol and propanol are markedly affected by the presence of traces of water. Although precautions to exclude traces of water were taken, there is no doubt that small amounts of water are absorbed, thus affecting the rates to a certain extent. Even traces of moisture resulted in a scattering in the log k against $1/T$ plot. However, the frequency factor and energy characteristics in propanol and ethanol are comparable to those in the methanol solutions. Although the energy of activation and frequency factor for the rate of isomerization of *cis*-$[Co(pn)_2Cl_2]Cl$ are higher in ethanol and propanol in comparison to the rates in methanol solutions, the degree of uncertainty of the rates in the first two solvents is greater.

The effect of LiCl on the rate of isomerization of *cis*-$[Co(pn)_2Cl_2]Cl$ in ethanol was studied. When proper precautions were not taken to exclude water from the solutions the rates were quite inconsistent, although they were of first order. When the absorption of water from the atmosphere was kept to a minimum, reasonably consistent values could be obtained. Lithium chloride exhibited a small negative salt effect. A definite mass effect was observed at the higher concentrations. The effect of perchlorate on the isomerization rate in ethanol could not be studied because of the insolubility of the *trans* isomer in this solvent.

The rate of isomerization of *cis*-$[Co(pn)_2Cl_2]Cl$ is first order with respect to the complex in propanol solutions containing lithium chloride. As in ethanol solutions, the rate is very sensitive to the presence of traces of water. The rate was 1.23×10^{-3} min.$^{-1}$ when the ratio of LiCl to complex was 1. The rate in pure propanol is 1.6×10^{-3} min.$^{-1}$ at 35.06°. As the ratio of LiCl to complex in propanol is increased to 36 the rate increases to 1.6×10^{-3} min.$^{-1}$. In each run the rate increased to almost twice the initial rate as the reaction neared completion at around 1100 minutes. This sudden increase probably is due to the absorption of a small amount of atmospheric water.

Discussion

The rates of isomerization of *cis*-dichlorobis-(propylenediamine)-cobalt(III) chloride and *cis*-dichlorobis-(ethylenediamine)-cobalt(III) chloride in the alcoholic solutions are of first order with respect to the complex, and zero order with respect to added chloride and perchlorate. The rates of the reactions in each solvent have frequency factors of 10^{12} to 10^{13} sec.$^{-1}$, and small positive entropies of activation. These conditions suggest that the isomerization is unimolecular and that the activated complex closely resembles the initial state of the reactant.[21]

The higher entropy of activation of *cis*-dichloro-bis-(propylenediamine)-cobalt(III) chloride in the alcohols, compared to that of the ethylenediamine complex, indicates the greater ease with which the former complex isomerizes in these solvents. The lower rate of the propylenediamine complex in ethanol and propanol, in comparison to the ethylenediamine complex in ethanol, arises from the higher energy of activation for the former two cases. The higher entropy of activation of the rate of isomerization of *cis*-$[\mathrm{Co(pn)_2Cl_2}]\mathrm{Cl}$ probably is due to the greater steric effect of the C-methyl group when the propylenediamine ligands are in *cis*-positions. A greater relative symmetry is obtained when the *trans* isomer is formed in the propylenediamine complex.

The progressively lower rates of isomerization of the complexes as the solvent proceeds from methanol to propanol cannot be explained by differences in dielectric constants. The rate of a first-order unimolecular reaction should be independent of the dielectric constant of the solvent. However, we may expect the activity coefficients of the initial and activated states to vary in different proportions in different solvents. In this case the rate might be expected to vary with the solvent since the rate for a first-order reaction is given by

$$v = kc_{\mathrm{A}}(f_{\mathrm{A}}/F_{\mathrm{X}})$$

The rates may also vary with different solvents due to ion-pair formation. Thus, a greater degree of ion-pair formation may be expected in a less polar solvent. The effects of ion-pair formation on the rates in aqueous solutions have been reported.[22,23] Positive evidence of ion-pair formation in alcoholic solutions of *cis*-$[\mathrm{Co(en)_2Cl_2}]\mathrm{Cl}$ and *cis*-$[\mathrm{Co(pn)_2Cl_2}]\mathrm{Cl}$ have been found by the present investigators.[24] The degree of ion-pair formation of the complexes increases as the solvent changes from methanol, ethanol to propanol.

The unimolecular mechanism of the isomerization of *cis*-$[\mathrm{Co(en)_2Cl_2}]\mathrm{Cl}$, as reported by Brown and Nyholm,[9] is represented by equation I. The steady-state treatment gives rise to the rate equation

$$-\frac{\mathrm{d}[cis]}{\mathrm{d}t} = \frac{k_1[cis]}{k_2/k_3 + 1}$$

where $[cis]$ is the concentration of the *cis* isomer. At low concentrations of chloride k_3 is much greater than k_2. However, at high concentrations of chloride k_2 becomes significant compared to k_3. Under these conditions the increasing ionic strength effect on the over-all rate is counteracted by the decreasing common-ion effect. The rate of isomerization at 25.00° reaches a maximum of 1.91×10^{-3} min.$^{-1}$ at a chloride to complex ratio of 69. As the chloride to complex ratio is increased to 165 the rate of isomerization decreases to 1.69×10^{-3} min.$^{-1}$. The highest ratio studied by Brown and Nyholm was 52.3 at 35.8°.

The negative salt effect of the rate of isomerization of *cis*-$[\mathrm{Co(pn)_2Cl_2}]\mathrm{Cl}$ in the alcohols suggests the formation of ion-pairs. Taube and Posey[22] have shown the formation of ion-pairs of the type $[\mathrm{Co(NH_3)_5(H_2O)}]^{+3}\mathrm{SO_4}^{=}$ in aqueous solutions. Dickens, Basolo and Neumann[23] have shown the negative salt effect of monovalent anions on the rate of dissociation of tris-(1,10-phenanthroline)-iron(III) complex. The formation of the ion-pairs have been attributed to the high charge on the central ion. It is evident that the tendency for ion-pair formation will increase with a high anion charge or a decrease in ionic radius. Due to the inductive effect of the C-methyl group in the propylenediamine ligand, it might be expected that there would be a greater effective positive charge on the central cobalt ion. This charge effect would result in the increased tendency toward ion-pair formation in the propylenediamine complex.

The following equilibria are considered

$$\begin{tikzcd}
\textit{Cis}\text{-}[\mathrm{Co(pn)_2Cl_2}]^{+}\mathrm{Cl}^{-} \arrow[r, shift left, "\mathrm{I}"] & \textit{cis}\text{-}[\mathrm{Co(pn)_2Cl_2}]^{+} + \mathrm{Cl}^{-} \arrow[l, shift left] \arrow[d, shift right, "\mathrm{II}\quad k_1"'] \\
\textit{trans}\text{-}[\mathrm{Co(pn)_2Cl_2}]^{+} & {[\mathrm{Co(pn)_2Cl}]^{+} + \mathrm{Cl}^{-}} \arrow[l, "k_3"'] \arrow[u, shift right, "k_2"']
\end{tikzcd}$$

From the rate equation for the isomerization of the *cis*-complex, it is noted that excess chloride ion causes a decrease in the concentration of *cis*-isomer as equilibrium I is shifted to the left; the result is a decrease in the rate of isomerization. The rate k_2 also becomes significant, relative to k_3, at high chloride concentrations, such that a common-ion effect is observed on the rate of isomerization.

In the presence of perchlorate, equilibria I and II are probably shifted to the left. These shifts could perhaps be visualized as arising from the weak association of perchlorate ions around the positions *trans* to the coördinated chloride on the negative perchlorate ion.

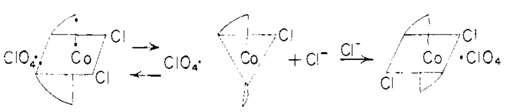
---

(21) Ref. 17, p. 296.

(22) H. Taube and F. A. Posey, THIS JOURNAL, **75**, 1463 (1953).

(23) J. E. Dickens, F. Basolo and H. M. Neumann, *ibid.*, **79**, 1286 (1957).

(24) Thesis, C. Hirayama, University of Minnesota, 1957.



The chloride ion approaching the penta-coördinated intermediate would have to penetrate the field due to the perchlorate in order to form the *trans*-isomer. If these conditions existed in the alcohol solutions, it is possible to account for the lower rate of isomerization in the presence of perchlorates. Initially, k_2 would be expected to be significant compared to k_3 because of the repulsive nature of the perchlorate ions on the negative ions, which results in the shift of equilibrium II toward the *cis*-dichloro complex. As the reaction progresses, the value of k_3 apparently contributes to such a point that the rate of isomerization attains a constant value.

The introduction of water into the system would tend to break up the ion pairs, such that the rates of isomerization increase. Such appears to be the case in the lithium chloride systems due to the high degree of hydration of this salt. In ethanol and propanol systems containing both lithium chloride and sodium perchlorate, a trace of water has a large affect. It should be noted that the activity coefficients in the presence of relatively high concentrations of salt are quite different from those in which there are no added ions.

MINNEAPOLIS, MINNESOTA

[CONTRIBUTION FROM WM. A. NOYES LABORATORY, UNIVERSITY OF ILLINOIS]

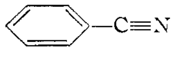
The Integrated Intensity of the Infrared C≡N Band of Benzonitriles in Various Solvents

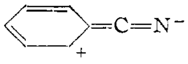
BY THEODORE L. BROWN

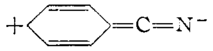
RECEIVED AUGUST 9, 1957

The integrated intensity of the infrared C≡N band for a group of substituted benzonitriles in various solvents has been studied. The magnitude of the intensity for any one compound is strongly dependent on the solvent, but the relative magnitudes within the series are not. The intensity is greatest for compounds containing the most electron-releasing substituents, suggesting a similarity between the C≡N stretching vibration and electrophilic rate processes. From the intensity results a set of reactivity constants is determined and compared with rate data taken from the literature.

Numerous studies of the infrared intensity of an absorption band possessed in common by a series of related molecules have shown that the variations of intensity within the series can be correlated with other molecular properties. These correlations are particularly good when the absorption is one which can be assigned in large measure to a localized functional group vibration. Among the functional group absorptions which have been studied in this way are the carbonyl,[1] aliphatic and aromatic hydroxyl,[2,3] and aliphatic and aromatic cyanides.[4] From intensity studies which have been made of functional groups attached to the phenyl ring it is clear that substituents on the ring exert a pronounced effect on the magnitude of the intensity. The direction of intensity change for a particular substituent compared with another is dependent on the nature of the functional group which is absorbing. For example, the OH intensity of *p*-nitrophenol is much greater than that of phenol, whereas the C≡N intensity of *p*-nitrobenzonitrile is lower than that of the unsubstituted molecule. The absorption intensity, A, is related by a proportionality constant to $(\delta\mu/\delta Q)^2$, where μ is the dipole moment of the molecule and Q is the vibrational coördinate. For vibrations which consist largely of a stretching motion along one bond axis, Q can be considered as the bond distance, r. It is frequently possible to fix the sign of the term $\partial\mu/\partial r$ from chemical or structural arguments. For example, the ground state of benzonitrile can be represented as a mixture of structures I, II and III; in the charge-separated canonical forms the carbon–nitrogen bond order is only two. It is to be expected, then, that as this bond distance increases during a stretching motion, the importance of the charge-separated forms increases, so that $\partial\mu/\partial r$ is then positive. Electron-releasing groups attached to the ring should facilitate this process; larger values of intensity are indeed observed for the more electron-releasing groups.[4]


I


II


III

While it is easy to understand the intensity variations from a qualitative point of view, quantitative relationships with other molecular properties are more difficult to establish. Nevertheless such relationships have been found for a few cases.[1,3,4] From consideration of the intensity results for a number of *m*- and *p*-substituted benzonitriles, Thompson and Steel have obtained a linear relationship between log A and the Hammett σ-constant of the substituent for the intensities measured both in carbon tetrachloride and in chloroform.[4] The slopes of the lines were surprisingly different, however, in the two solvents. There is also some question as to the significance of the linear relationship which was obtained. Log A is not related from theory in a simple way to any other molecular properties, so that the use of this function would appear to be for reasons of utility only. Furthermore, there is considerable evidence that the use of the Hammett σ-values is inappro-

---

[1] G. M. Barrow, *J. Chem. Phys.*, **21**, 2008 (1953).

[2] T. L. Brown and M. T. Rogers, THIS JOURNAL, **79**, 577 (1957).

[3] T. L. Brown, *J. Phys. Chem.*, **61**, 820 (1957).

[4] H. W. Thompson and G. Steel, *Trans. Faraday Soc.*, **52**, 1451 (1956).