in the presence of PMES, while the corresponding values in the presence of PVS are 0.08, 0.30, and 0.66, respectively. It appears then that the reagent ions are in all cases more strongly bound than the alkaline earth ions.

Temperature Dependence of Polyion-Catalyzed Reaction. The analysis outlined in the previous section shows that, under conditions where all reagent ions are bound to the polymer domain, the catalytic effect depends on the high values of $C_{\text{eff}}^{\max}$, which would be expected to be practically independent of temperature. We should then expect that at high polyion concentrations the activation energy is very similar to that characterizing the reaction in the absence of the polyion. On the other hand, at low polyion concentration the fraction of reagent ions bound would be expected to be temperature dependent and the activation energy may be significantly affected by the polyion. Specifically, using the formulation of eq 7

$$\Delta E^*_{\text{cat}} = \Delta E^*_0 - 2\Delta H_{\text{d}} \qquad (11)$$

where ΔE^*_{cat} and ΔE^*_0 are the activation energies in the presence and the absence of catalytic polyion and ΔH_{d} is the enthalpy of dissociation of the polyion–reagent ion complex. It was expected that this dissociation would be endothermic, so that $\Delta E^*_{\text{cat}} < \Delta E^*_0$ at low polyion concentrations. Table V is in agreement with these expectations in that the ΔE^* tend to increase with polymer concentrations. With PMES catalysis, the ΔE^* values come, at $C_p = 1.5 \times 10^{-3}$ N, to within 1.4 kcal/mole of the value characterizing the reaction in the absence of polymer. With PVS, on the other hand, the activation energy remains low even at very high polymer concentrations, suggesting perhaps that the change in the nature of the reaction medium, when the reagent ions enter the polyion domain, produces significant changes in the activation process.

Table V. Temperature Dependence of the Reaction of $Co(NH_3)_5Cl^{2+}$ with Hg^{2+} in the Presence and Absence of Polymer

Polymer	Temp, °C	10^5C_p	10^5 (Hg^{2+})	$(NaClO_4)$	10^4k_1	ΔE^*, kcal/mole
None	35	0	50	0.01	0.78	
	48	0	50	0.01	3.06	
	55	0	50	0.01	5.85	
	62	0	50	0.01	10.3	19.6
PMES	5	5	50	0.03	5.95	
	25	5	50	0.03	25.6	12.0
	5	5	5	0.01	12.6	
	25	5	5	0.01	62.5	13.2
	5	50	5	0.01	22.2	
	25	50	5	0.01	149	16.0
	5	150	5	0.01	7.3	
	25	150	5	0.01	65.7	18.1
PVS	5	5	5	0.03	30.9	
	25	5	5	0.03	155	13.3
	5	300	5	0.03	18.6	
	25	300	5	0.03	129	15.7

Kinetics of Structural Interconversions. I. Cobalt(II) Chloride–Pyridine–Nitromethane

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Abstract: A kinetic examination of the $^{\text{oct}}Co(py)_4Cl_2 = {}^{\text{tet}}Co(py)_2Cl_2 + 2py$ equilibrium in nitromethane and pyridine (py) has been carried out. The experimental data appear to fit the mechanism, $Co(py)_4Cl_4 \rightleftharpoons Co(py)_3Cl_2 + py$ (3) and $Co(py)_3Cl_2 \rightleftharpoons Co(py)_2Cl_2 + py$ (k_4, k_{-4}) (4), where reaction 3 equilibrates rapidly compared to reaction 4. The rate constant k_{-4} in nitromethane at $\mu = 0.1$ (Et_4NClO_4) and 25.0° is $(7.2 \pm 0.5) \times 10^4$ M^{-1} sec^{-1}, and $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ are 5.4 ± 0.8 kcal/mole and −18 ± 3 eu, respectively. The corresponding rate constant in pyridine is $(3.1 \pm 0.3) \times 10^3$ M^{-1} sec^{-1}, and the activation parameters are 2.6 ± 1.0 kcal/mole and −34 ± 4 eu. Factors affecting the kinetics in the two solvents are discussed.

Equilibria between structural isomers of inorganic complexes in nonaqueous solvents are well known, and the subject has been recently reviewed by Katzin.[1] Configurational equilibria between octahedral and tetrahedral or square-planar cobalt(II) complexes have been reported.[1,2] Specifically, thermodynamic and spectral data have been obtained for a number of octahedral (oct)–tetrahedral (tet) equilibria of the type

$$^{\text{oct}}CoL_4X_2 = {}^{\text{tet}}CoL_2X_2 + 2L \qquad (1)$$

where L = pyridine or 2-methylpyridine and $X^- = Cl^-$, Br^-, I^-, OCN^-, SCN^-, and $SeCN^-$. In the case where L = pyridine (py) and $X^- = Cl^-$, data have been obtained in a number of organic solvents.[3-5] However, to our knowledge no kinetic studies have been made on these systems. The large enthalpy and spectral changes accompanying the octahedral–tetrahedral interconversion make these systems feasible for temperature-jump relaxation studies. In the present work we have investigated the kinetics of the octahedral-tetrahedral interconversion

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(1) L. I. Katzin in "Transition Metal Chemistry," Vol. 3, R. L. Carlin, Ed., Marcel Dekker, Inc., New York, N. Y., 1966, pp 56–86.

(2) G. W. Everett, Jr., and R. H. Holm, *J. Am. Chem. Soc.*, **87**, 5266 (1965), and references therein.

(3) H. C. A. King, E. Körös, and S. M. Nelson, *J. Chem. Soc.*, 5449 (1963).

(4) W. Libuš and I. Uruska, *Inorg. Chem.*, **5**, 256 (1966).

(5) L. I. Katzin, *J. Chem. Phys.*, **35**, 467 (1961).

$$^{oct}Co(py)_4Cl_2 = {}^{tet}Co(py)_2Cl_2 + 2py \qquad (2)$$

in nitromethane and pyridine. In addition the effects of chloride and water on the kinetics are also examined. Some spectral and equilibrium data are presented.

Experimental Section

Materials. Baker analyzed reagent grade cobalt(II) chloride hexahydrate was used to prepare the complex $Co(py)_2Cl_2$,[6] which was the source of cobalt(II) in the experiments. The spectrum of $Co(py)_2Cl_2$ in nitromethane was in complete agreement with that reported by Nelson and coworkers.[3] Pyridine and nitromethane were spectroquality solvents purchased from Allied Chemicals and Matheson Coleman and Bell, respectively. Both solvents were purified by distillation after storage with Linde Type 4A molecular sieves. The water concentrations in pyridine and nitromethane after purification, as determined *via* the Karl Fischer method, were 0.010 and 0.029 *M*, respectively. Tetraethylammonium perchlorate and chloride were obtained from Eastman Organic Chemicals. The salts were reagent grade and were used without further purification after drying under vacuum at 100° for 2 hr. The water content of pyridine and nitromethane solutions 0.1 *M* in Et_4NClO_4 were 0.014 and 0.033 *M*, respectively, using the Karl Fischer titration technique.

Kinetic Experiments. The temperature-jump relaxation technique has been described elsewhere.[7] The instrument used in this study was manufactured by the Messanlagen Studiengeschellschaft, G.m.b.H., Goettingen, Germany. The solution temperature was increased by discharging a condenser charged to 30 kV through a cell containing a solution 0.1 *M* in either Et_4NClO_4 and/or Et_4NCl.

The resulting temperature change was measured by a direct technique. The light transmission from nitromethane–pyridine and pyridine solutions containing cobalt(II) chloride and inert electrolyte was measured at the initial temperature and at temperatures up to 5° higher for each experiment. The light transmission was recorded as a voltage measurement on an oscilloscope. The temperatures were measured with a copper–constantan thermocouple used in conjunction with a Leeds and Northrup millivolt potentiometer. The solution was returned to the initial temperature used in the experimental measurement to check lamp stability, and the temperature perturbation was applied. The voltage change that occurred was transformed into a temperature change from the calibration curve (oscilloscope voltage as a function of temperature). The temperature changes in nitromethane–pyridine and pyridine solutions were 3.6 ± 0.1 and 3.5 ± 0.1°, respectively, over the range of temperatures used for the kinetic measurements.

The concentration changes resulting from the temperature perturbation were followed spectrally in the 560–595-mμ region. For changes in concentration near equilibrium

$$d\Delta C/dt = -(1/\tau)\Delta C$$

where ΔC is the concentration difference between a given time and infinite time (concentration at perturbed temperature) and τ is the relaxation time. The relaxation time was measured from the traces of light transmission *vs.* time recorded on an oscilloscope. Each value of τ is the average of at least two measurements. A Teflon temperature-jump cell was used, and the solutions were equilibrated at least 30 min prior to the actual jump. The effects of cobalt(II), pyridine, water, and chloride ion on the kinetics were examined. The magnitude of the relaxation effect for solutions of about the same light transmission decreased with decreasing pyridine concentrations in nitromethane, and no relaxation effect was observed for nitromethane solutions containing only $Co(py)_2Cl_2$ with no added pyridine. This eliminated cavitation or related effects as the source of the observed voltage change. Density corrections of the solvents were made where necessary in determining concentrations at the different temperatures.

Equilibrium Experiments. Equilibrium constants for reaction 2 in nitromethane were determined spectrophotometrically using a Cary Model 14 recording spectrophotometer (Applied Physics Corp.) equipped with a thermostated cell holder for maintaining temperature control of the solutions. To obtain the equilibrium constants, a series of solutions of known cobalt(II) concentration ($1-2 \times 10^{-3}$ *M*) was prepared containing different known amounts of pyridine (0.5–3.0 *M*). The equilibrium concentration of the tetrahedral species was obtained from a previously determined calibration curve relating $Co(py)_2Cl_2$ to absorbance in nitromethane where it is assumed that only $^{tet}Co(py)_2Cl_2$ is present. This method is similar to that used by other workers.[3] Equilibrium constants were measured at 7.0, 16.5, and 25.0°. The temperatures were measured to within ±0.5° from calibrated thermometers.

The room-temperature spectrum of cobalt(II) chloride in pyridine is predominantly that of the octahedral complex $Co(py)_4Cl_2$ although some of the tetrahedral complex $Co(py)_2Cl_2$ is also present. When 10^{-2} *M* Cl^- is added to a 10^{-3} *M* solution of cobalt(II) chloride in pyridine, there is an increase in intensity and shift to longer wavelengths (600, 637, and 665 mμ) of the spectral bands compared to those of $Co(py)_2Cl_2$ (572, 608, and 637 mμ). This spectral change is believed to be due to formation of the $Co(py)Cl_3^-$ species.[8] When the chloride concentration is increased from 10^{-2} to 1.0 *M*, spectra of the resulting solutions show that there is an additional increase in the intensity of the spectral bands at the longer wavelengths (600, 637, and 665 mμ). If a solution 1.0 *M* in chloride (approximate solubility limit of tetraethylammonium chloride in pyridine) and 10^{-3} *M* in cobalt(II) is heated, there is a further increase in absorbance at the wavelengths mentioned above. These results show that increasing the chloride concentration and temperature favors formation of the tetrahedral species, $Co(py)Cl_3^-$. Spectrophotometric measurements relating to the enthalpy of the equilibrium involving cobalt(II) chloride in pyridine with added chloride were determined in a manner analogous to that used by other workers.[3,8]

Chloride was also added to 10^{-3} *M* $Co(py)_2Cl_2$ in nitromethane with spectral results similar to those obtained in pyridine. There were spectral shifts to longer wavelengths accompanying the increased intensity of the absorbance bands as the chloride concentration was increased. Introduction of pyridine shifted the bands to shorter wavelengths with a corresponding decrease in absorbance. The spectrum of the solution at high chloride concentrations (~0.1 *M*) was identical with that of $CoCl_4^{2-}$.[9] The shift of the isosbestic point of $Co(py)_2Cl_2$ and the higher chlorinated cobalt species with increased chloride concentration indicates more than two tetrahedral species may be present in solution. These results suggest that the following equilibria are present in nitromethane.

$$Co(py)_2Cl_2 + Cl^- \rightleftharpoons Co(py)Cl_3^- + py$$

$$Co(py)Cl_3^- + Cl^- \rightleftharpoons CoCl_4^{2-} + py$$

Results

Kinetic Measurements in Nitromethane. The equilibrium for cobalt(II) chloride in pyridine and pyridine–nitromethane solutions is represented by reaction 2 with the equilibrium concentration quotient for reaction 2 defined as K_2. This equilibrium is supported by both conductivity and spectral measurements made in the above solutions.[3,5] Kinetic measurements of reaction 2 gave results which are consistent with a stepwise mechanism with reaction 3 equilibrating rapidly compared to reaction 4. Only one relaxation was observed with the temperature-jump apparatus and this occurred in the microsecond time range. The observable relaxation is believed to be attributed to reaction 4 coupled to reaction 3. Assuming the proposed pentacoordinated intermediate is present in undetectable small amounts, the relaxation expression derived in the manner analogous to that of Amdur and Hammes[10] is shown in (5).

$$^{oct}Co(py)_4Cl_2 \underset{k_{-3}}{\overset{k_3}{\rightleftharpoons}} Co(py)_3Cl_2 + py \qquad K_3 \qquad (3)$$

$$Co(py)_3Cl_2 \underset{k_{-4}}{\overset{k_4}{\rightleftharpoons}} {}^{tet}Co(py)_2Cl_2 + py \qquad K_4 \qquad (4)$$

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[6] N. S. Gill, R. S. Nyholm, G. A. Barclay, T. I. Christie, and P. J. Pauling, *J. Inorg. Nucl. Chem.*, **18**, 88 (1961).

[7] M. Eigen and L. DeMaeyer in "Techniques of Organic Chemistry," Vol. VIII, Part II, A. Weissberger, Ed., Interscience Publishers, Inc., New York, N. Y., 1963, Chapter XVIII.

[8] D. E. Scaife and K. P. Wood, *Inorg. Chem.*, **6**, 358 (1967).

[9] N. S. Gill and R. S. Nyholm, *J. Chem. Soc.*, 4000 (1959).

[10] I. Amdur and G. G. Hammes, "Chemical Kinetics: Principles and Selected Topics," McGraw-Hill Book Co., Inc., New York, N. Y., 1966, p 141.

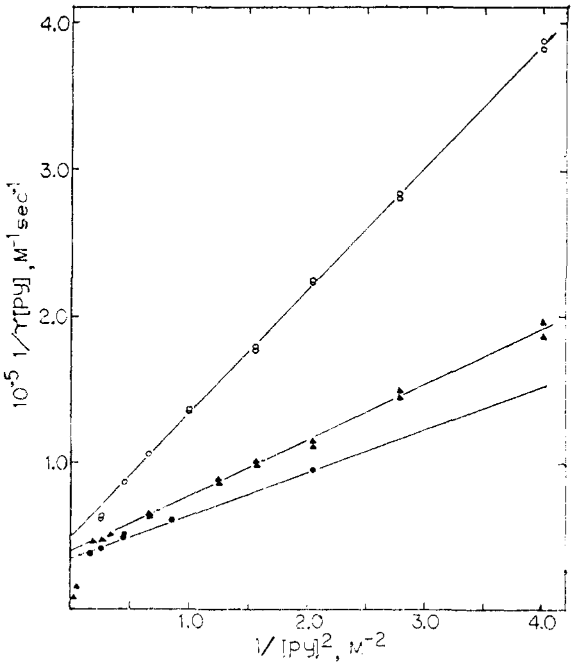

Figure 1. Plot of $1/(\tau[\mathrm{py}])$ *vs.* $1/[\mathrm{py}]^2$. Solvent, nitromethane; $\mu = 0.1$ (Et_4NClO_4); temperatures: ○, 16.0°; ▲, 8.6°; and ●, 4.6°.

$$1/\tau[\mathrm{py}] = k_{-4} + (k_4K_3/[\mathrm{py}]^2) \qquad (5)$$

Figure 1 is a plot of $(\tau[\mathrm{py}])^{-1}$ *vs.* $[\mathrm{py}]^{-2}$ which gives a straight line with a slope of k_4K_3 and an intercept of k_{-4}. Linear plots were obtained at pyridine concentrations of less than 5.0 *M*. However, when the concentrations were increased to 5.0 *M* or greater, deviations from linearity occurred. Presumably this reflects the influence of pyridine as a solvent on the rate. The values of k_{-4} and k_4K_3 at various temperatures are: $3.5 \pm 0.3 \times 10^4$ M^{-1} sec^{-1}, $2.8 \pm 0.1 \times 10^4$ *M* sec^{-1} (4.6°); $4.0 \pm 0.2 \times 10^4$, $3.8 \pm 0.1 \times 10^4$ (8.6°); and $5.2 \pm 0.2 \times 10^4$, $8.3 \pm 0.2 \times 10^4$ (16.0°) at $\mu = 0.1$ (Et_4NClO_4). From a plot of ln (k_{-4}/T) *vs.* $1/T$ the activation parameters $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ were 5.4 + 0.8 kcal/mole and −18 ± 3 eu, respectively. Neither k_4 nor K_3 are known. Therefore an alternate expression was used from the relationship that the over-all equilibrium constant, K_2, is equal to the product K_3K_4. Thus $k_4K_3 = k_{-4}K_2$ from which the over-all equilibrium constant, K_2, was determined. The values of K_2(spectral) and K_2(kinetic) respectively at various temperatures are: 0.70 M^2, 0.79 M^2 (4.6°); 0.98, 0.95 (8.6°); and 1.80, 1.64 (16.0°). There was fair agreement between the two methods.

The effect of cobalt(II) concentration on the relaxation time was examined over a concentration range of 2×10^{-3}–10^{-2} *M*. This range is limited by the spectral changes observable with the temperature-jump apparatus. Examination of Table I shows that the relaxation time was independent of cobalt(II) concentration. The relaxation time in pyridine–nitromethane was unaffected by water concentrations of 0.5 *M* or less. However, at higher concentrations (~0.9 *M*), the relaxation time decreased. This could be attributed to a number of factors. Introduction of water may effect the specific solvation of both the cobalt(II) complexes and pyridine. Moreover, the amount of water, although small in comparison with nitromethane, is appreciable with respect to the amount of pyridine and chloride present. This in turn could cause possible alteration of the inner coordination spheres of the cobalt complexes. Water with its base strength and high dielectric constant promotes dissociation of the octahedral complex $Co(py)_4Cl_2$.[11] At fairly high water concentrations (~6 *M*) there was complete collapse of the tetrahedral and octahedral pyridine complexes as evidenced by the oily pink solution which probably results from formation of aqueous cobalt(II) complexes.

Table I. Effect of Water and Cobalt Concentrations on Relaxation Rates in Nitromethane[a]

10^3[Co(II)],[b] *M*	[H_2O], *M*	Temp, °C	$10^{-4}(1/\tau)$,[c] sec^{-1}
2.0	. . .	8.6	9.2
4.9	. . .	8.6	9.6
10.0	. . .	8.6	9.6
10.0	0.03	16.0	12.8
10.0	0.48	16.0	12.1
10.0	0.93	16.0	95.3

[a] $\mu = 0.1$ (Et_4NClO_4), [py] = 2.0 *M*. [b] $Co(py)_2Cl_2$ source of cobalt(II). [c] Average of two measurements.

Kinetic Measurements in Pyridine. The over-all equilibrium constant in pyridine for the octahedral–tetrahedral interconversion as measured by Katzin[5] is estimated as 6.1 M^2 at 38°. This is smaller than the extrapolated value in nitromethane by a factor of 1.6. In pyridine, the octahedral complex is favored as evidenced by the spectra of the magenta-colored solution, whereas in pyridine–nitromethane the tetrahedral complex is favored as noted by the intense blue color of the solution. In both media the tetrahedral complex is favored at higher temperatures. The relaxation times at a given temperature were found to be significantly larger than in nitromethane. The reciprocal of the relaxation time as a function of temperature was $2.9 \pm 0.3 \times 10^4$ sec^{-1} (12.4°), $3.8 \pm 0.2 \times 10^4$ (23.4°), $4.1 \pm 0.2 \times 10^4$ (27.9°), and $4.7 \pm 0.3 \times 10^4$ (38.4°) at [Co(II)] = 1.0×10^{-2} *M* and $\mu = 0.1$ (Et_4NClO_4). Rearranging eq 5 to include the over-all equilibrium constant leads to

$$\tau^{-1} = k_{-4}\{[\mathrm{py}] + (K_2/[\mathrm{py}])\} \sim k_{-4}[\mathrm{py}] \qquad (6)$$

where the relaxation expression can be approximated by k_{-4}[py]. The value of k_{-4} obtained in pure pyridine is 2.3×10^3 M^{-1} sec^{-1} at 12.4° or a factor of 20 less than in nitromethane. This of course assumes no mechanistic change occurs in the two solvents. A plot of ln (k_{-4}/T) *vs.* $1/T$ yielded a straight line with the activation parameters $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ being 2.6 ± 1.0 kcal/mole and −34 ± 4 eu, respectively. The smaller rate constant in pyridine is due to the less favorable activation entropy associated with the reaction in this solvent. The concentration of cobalt(II) was varied over an order of magnitude (10^{-3}–10^{-2} *M*) with no appreciable effect on the relaxation time as was the case in nitromethane. Chloride was then added and the solution immediately assumed an intense aqua color. Spectra of the resulting solutions show a shift and intensification of the peaks to longer wavelengths. The bands at 600, 637, and 665 mμ are probably due to the tetrahedral cobalt complex,

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[11] L. I. Katzin, *J. Chem. Phys.*, 36, 3034 (1962).

$Co(py)Cl_3^-$.[8,12] The high base strength of pyridine is believed to stabilize the octahedral complex against transformation to the tetrahedral species. However, in the presence of added chloride, the ${}^{tet}Co(py)Cl_3^-$ species forms, as was postulated by Scaife and Wood[8] for some cobalt and nickel halides in water and alcohols, the reaction being

$$Cl^- + {}^{oct}Co(py)_4Cl_2 \rightleftharpoons {}^{tet}Co(py)Cl_3^- + 3py \qquad (7)$$

It is less likely that there is any contribution from $CoCl_4^{2-}$ since studies in acetone showed that a single equivalent of pyridine was able to displace one of the chlorides in $CoCl_4^{2-}$ even with LiCl in excess.[5] Added chloride concentrations up to 10^{-2} *M* showed no influence on the observed relaxation time. This suggests that either the substitution rate of pyridine on the tetrahedral cobalt complexes ${}^{tet}Co(py)_2Cl_2$ and ${}^{tet}Co(py)Cl_3^-$ is essentially the same within experimental error or that equilibrium 2 is still being observed despite the presence of chloride as ΔH_2 is very much larger than ΔH_8. Subsequent studies on the analogous bromide systems show the latter explanation to be the correct one.

The chloride effect could not be studied in nitromethane since jumps made on this solution produced cavitation. Evidently the conductance of the nitromethane solution is sufficiently affected to prevent measurement with the temperature-jump apparatus. Possibly ion pairing occurs which results in a decreased conductivity of the solution. No such problem seems to exist in pyridine.

Equilibrium Measurements in Nitromethane and Pyridine. The equilibrium constants in nitromethane which were determined spectrophotometrically, K_2(spectral), at different temperatures were used in determining the ΔH of the octahedral–tetrahedral interconversion (reaction 2). A plot of log K_2 *vs.* $1/T$ yielded a ΔH of 13.3 kcal/mole. This result was within experimental error of the value obtained by Katzin for the same interconversion in pyridine.[5] The equilibrium constants determined in this study were obtained at an ionic strength of 0.1 (Et_4NClO_4). The equilibrium constant determined by Nelson and coworkers[3] at 20° in this solvent with no added electrolyte was in excellent agreement with the value extrapolated from our data. This shows that ionic strength does not have an appreciable effect on the equilibrium constant in nitromethane.

The values of ΔH for reaction 7 obtained from a plot of the peak intensities at 665 and 600 mμ *vs.* reciprocal absolute temperature were in excellent agreement and found to be 15.8 and 15.4 kcal/mole, respectively. It is interesting to note the small ΔH resulting from chloride substitution of a tetrahedral cobalt complex. Since the enthalpy change is a thermodynamic function independent of the path, reaction 7 can be expressed as the sum of reactions 2 and 8 as follows.

$${}^{oct}Co(py)_4Cl_2 \rightleftharpoons {}^{tet}Co(py)_2Cl_2 + 2py \qquad \Delta H_2 \qquad (2)$$

$${}^{tet}Co(py)_2Cl_2 + Cl^- \rightleftharpoons {}^{tet}Co(py)Cl_3^- + py \qquad \Delta H_8 \qquad (8)$$

The ΔH for reaction 7 is simply equal to the sum of ΔH_2 and ΔH_8. The value of ΔH_2 as determined previously by Katzin is 13.4 kcal/mole. Therefore ΔH_8 is of the order of 2–2.4 kcal/mole.

Discussion

Kinetic Data. Recent studies[13] on a number of cobalt(II) systems in nonaqueous solvents have shown that the quadricoordinated cobalt(II) complex may also assume a square-planar configuration. In view of this, a mechanism was tested whereby a square-planar intermediate (sq) is assumed. The mechanism is as indicated below

$${}^{oct}Co(py)_4Cl_2 \underset{k_{-9}}{\overset{k_9}{\rightleftharpoons}} {}^{sq}Co(py)_2Cl_2 + 2py \qquad K_9 \qquad (9)$$

$${}^{sq}Co(py)_2Cl_2 \underset{k_{-10}}{\overset{k_{10}}{\rightleftharpoons}} {}^{tet}Co(py)_2Cl_2 \qquad K_{10} \qquad (10)$$

Assuming step 9 occurs rapidly and that the square-planar intermediate is present in undetectable small amounts, the relaxation time becomes

$$\tau^{-1} = k_{-10} + (k_{10}K_9/[py]^2)$$

A plot of τ^{-1} *vs.* $[py]^{-2}$ was nonlinear and hence the mechanism was discarded.

Another mechanism is one in which reaction 3 equilibrates slowly compared to reaction 4. In this case

$$\tau^{-1} = k_3 + (k_{-3}/K_4)[py]^2$$

which does not conform with the experimental data and was therefore discarded.

The compound $Co(py)_2Cl_2$ exists in two different forms which differ markedly in color and other physical properties. These are the violet (stable) form which is an octahedral polymer[14] and a blue unstable form which is a tetrahedral monomer.[6] Therefore in solution an equilibrium involving an octahedral polymer–tetrahedral monomer might certainly be plausible. However, the relaxation time was independent of cobalt concentration and inversely dependent on the pyridine concentration which rules out this mechanism. There are many other reaction schemes that might be proposed, but at present the stepwise mechanism involving a pentacoordinate intermediate is entirely satisfactory and consistent with the experimental results. Pentacoordinated cobalt(II) complexes although uncommon are known, and recent evidence has been obtained from a number of systems to support this coordination number.[15]

Examination of the literature shows that there are very few papers dealing with the substitution rates of tetrahedral cobalt complexes. One paper discusses ligand exchange with some tertiary phosphine complexes of cobalt(II) in deuteriochloroform[16] while another examines the kinetics of the tetrahedral–octahedral interconversion of the aquocobalt(II) complex.[17] The results of the latter work indicate that the interconversion is slow. To test whether the substitution rate of a tetrahedral cobalt(II) complex is too slow for temperature-jump studies, 5 × 10^{-3} *M* $Co(py)_2Cl_2$ solutions were rapidly mixed with 5 × 10^{-3} *M* chloride solutions in nitromethane and in pyridine on the stopped-flow apparatus at 25°. Introduction of halide to the cobalt-

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(12) L. I. Katzin and E. Gebert, *J. Am. Chem. Soc.*, **72**, 5464 (1950).

(13) G. W. Everett, Jr., and R. H. Holm, *ibid.*, **88**, 2442 (1966).

(14) J. D. Dunitz, *Acta Cryst.*, **10**, 307 (1957).

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(17) T. J. Swift, *Inorg. Chem.*, **3**, 526 (1964).

(II) complex in nitromethane and pyridine produces an increase in the intensity of the spectral bands and a shift to longer wavelengths as was previously discussed. Spectral analysis indicates that higher chloride-substituted tetrahedral complexes are formed. Chloride substitution occurs with a half-life of less than 0.1 sec. The rate constant for the reactions of Cl^- with $Co(py)_2Cl_2$ is greater than 4×10^3 M^{-1} sec^{-1} at 25° in both solvents. This result shows that the rate of pyridine substitution of the tetrahedral complex is less than that of chloride in the pyridine solvent.

From the temperature-jump studies k_{-4} at $\mu = 0.1$ (Et_4NClO_4) and 25° is 7.2×10^4 M^{-1} sec^{-1} (nitromethane) and 3.1×10^3 M^{-1} sec^{-1} (pyridine). This order of magnitude is in reasonable agreement with the results of the ligand-exchange study in deuteriochloroform.[16] The rapid rate of substitution of the tetrahedral cobalt complex is not too unexpected as crystal field theory predicts a favorable crystal field activation energy for formation of the pentacoordinated activated complex from the tetrahedral complex whether it be a trigonal bypyramid or a square pyramid with the latter configuration being less favored. It is well understood that this is not the only factor to be considered. Electrostatic effects are also important and difficult to assess as we are dealing with uncharged reactants except in the few experiments involving the $Co(py)Cl_3^-$ species. Amis[18] has developed a simplified relationship between the rate constant and dielectric constant of the solvent for dipole–dipole interactions of dipolar reactants, and in the case of a head-on alignment this becomes

$$\ln k_D = \ln k_\infty - (2\mu_1\mu_2/kTDr^3) \qquad (11)$$

where r is the distance of approach of the two dipoles μ_1 and μ_2. The dipole moments of pyridine and $Co(py)_2Cl_2$ were taken as 2.2[19] and 12 D,[20] respectively. Using the measured values of the rate constants in pyridine and nitromethane and rearranging eq 11 leads to

$$\ln (k_{\text{nitromethane}}/k_{\text{pyridine}}) = \frac{2\mu_1\mu_2}{kT}\left[\frac{1}{D_{py}r_{py}^3} - \frac{1}{D_{NM}r_{NM}^3}\right] \qquad (12)$$

where the dielectric constants of nitromethane and pyridine are known.[1] Assuming that the distance of approach, r, is the same in the two solvents, a value of about 3 Å is obtained. This value of r is low, perhaps by a factor of 3, but the result is not too surprising since the rate difference in the two solvents is attributed to electrostatic effects alone. Other factors affecting the rate are also important, such as differences in the specific solvation of the reactants in the two solvents.

An equation has been developed for the free energy of activation of dipoles in a medium of a given dielectric constant.[21] This relationship predicts that, if the bimolecular rate constant k_{-4} increases with increasing dielectric constant of the medium, the entropy of activation arising from the interaction of the dipoles will be negative. This is the case observed for the experiments reported in this paper. Since there may be several factors which contribute to the enthalpy and entropy of activation, it is very difficult to assess in detail the specific effects responsible for the difference of $\Delta H^\ddagger$ and $\Delta S^\ddagger$ in the two solvents. However, Basolo and Pearson in studies of the substitution reactions of square-planar platinum(II) complexes point out that fairly large negative entropies and rather small enthalpies of activation suggest that formation of the activated complex is accompanied by a net increase in bonding.[22] Applying this reasoning to our system lends some support for the proposed five-coordinated intermediate.

Acknowledgment. The authors wish to thank the Petroleum Research Fund of the American Chemical Society through Grant PRF-2177-A3,5 for their support of this work.

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