

Mechanism and Kinetics of Ligand Exchange in Co(II) Complexes of Thiourea

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The kinetics of ligand exchange of eight Co(II) complexes of thiourea and substituted thioureas have been measured. In each case two mechanisms are involved. The first is a direct associative exchange and the second requires initial displacement of thiourea by the solvent (acetone). Rate constants and activation parameters are presented. The lability of the complexes arises from the low enthalpies of activation.

Introduction

Ligand exchange is a process fundamental to all of coordination chemistry and as such has been the subject of intensive investigation.¹ However a large proportion of the papers in the literature have been concerned with complexes of Cr(III), Co(III) and Pt(II) in aqueous solution for which the rates of exchange are relatively slow and the exchange processes are amenable to study by classical methods. Our interest is in labile complexes in non-aqueous solution since these processes are more pertinent to the understanding of the mechanisms of homogeneous catalysis. Previous research in this area is relatively restricted. We are particularly interested in enquiring how the ligand exchange rates vary with changes in transition metal ion, in geometry, in substituent on the exchanging ligand, and in the nature of the non-exchanging ligands. We have therefore undertaken a fairly extensive study of ligand exchange processes of complexes of thiourea and substituted thioureas with first row transition metal ions. Some of the reasons for choosing this particular set of complexes have been outlined in a previous paper² which presented the results of a qualitative NMR study of a number of Co(II) complexes of thiourea. The present paper is concerned with quantitative measurements on the ligand exchange reactions of these same complexes. In subsequent papers ligand exchange in these cobalt complexes will be compared with those in thiourea complexes of nickel and zinc.

All of the cobalt thiourea complexes to be discussed have tetrahedral or distorted tetrahedral geometry in solution.² Ligand exchange studies have previously been reported for three series of tetrahedral cobalt complexes. All of these studies have used NMR to ob-

tain rate data. This technique has also been used in the present work.

Pignolet and Horrocks^{3,4} have examined the ligand exchange reactions of CoL_2X_2 complexes where L is a phosphine and X a halide ion. They found a second order (associative) exchange mechanism and report enthalpies of activation in the range 5–10 Kcal and entropies of activation in the range –20 to –30 e.u. We will compare these results with those obtained with analogous thiourea complexes later in the present paper. Zumdahl and Drago⁵ have studied a similar series of hexamethyl phosphoramidate complexes. Measurements on these compounds were restricted by the narrow temperature range accessible for study. However, they were able to demonstrate both a second order exchange process with an activation energy of around 5 Kcal and a first order process with a higher activation energy of around 15 Kcal. They considered that this second process indicated a dissociative mechanism involving a three coordinated cobalt intermediate. The same authors⁶ have also studied the kinetics of ligand exchange in CoL_2Cl_2 (L = 2-picoline) and found an associative process with $\Delta H^\ddagger = 4.8$ Kcal, $\Delta S^\ddagger = -14.5$ e.u. Thus it appears from these studies that associative kinetics predominate with rather small enthalpies of activation and rather large negative entropies of activation but that there is a possibility of a first order exchange process.

NMR studies

In an earlier paper² we reported the NMR spectra of a variety of Co(II)thiourea complexes. In each case the thiourea ligands are clearly exchanging rapidly on the NMR time scale at room temperature but slowly at –80°C. Equilibrium constants for the replacement of thiourea by the solvent (acetone) were also reported. The situation is clearly favourable for obtaining rate data from NMR measurements but some care in the choice of experimental method is necessary. In principle the NMR spectra provide rate information over the complete temperature range from very slow to very fast ligand exchange and a spectrum obtained at any temperature can be fitted to a computer simula-

tion generated by appropriate choices of rate and equilibrium constants. In these paramagnetic complexes, though, the chemical shifts are very large and the lines inherently relatively broad. As a result, in the intermediate ligand exchange region the intensity of a resonance is spread over as much as several thousand Hz and the quality of the spectra in terms of signal to noise ratio is not such as to encourage reliance of fitting to a computer simulation. As a result we are restricted to the use of the low temperature (slow exchange) and high temperature (fast exchange) regions. Reasonable approximations are available relating the lifetimes in the different environments to the observed line widths. For slow exchange:

$$\frac{1}{T_{2A'}} = \frac{1}{T_{2A}} + \frac{1}{\tau_A} \quad \text{and} \quad \frac{1}{T_{2B'}} = \frac{1}{T_{2B}} + \frac{1}{\tau_B} \quad (1)$$

where $\frac{1}{T_{2A'}}$ and $\frac{1}{T_{2B'}}$ are obtained from the measured line widths for protons at sites A and B, T_{2A} and T_{2B} are the nuclear spin relaxation times at sites A and B and τ_A and τ_B are the corresponding lifetimes associated with the chemical exchange process. In the fast exchange region the appropriate relation is:

$$\frac{1}{T_2'} = \frac{P_A}{T_{2A}} + \frac{P_B}{T_{2B}} + P_A^2 P_B^2 (\omega_A - \omega_B)^2 (\tau_A + \tau_B) \quad (2)$$

In this case $\frac{1}{T_2'}$ is obtained from the measured line width of the averaged resonance, P_A and P_B are the fractions of protons in sites A and B respectively and $\omega_A - \omega_B$ is the chemical shift difference between the two sites. P_A , P_B and $(\omega_A - \omega_B)$ are known as a function of temperature from the equilibrium constants and limiting shift data reported previously. Combination of equation (2) with the relationship:

$$\frac{\tau_A}{\tau_B} = \frac{P_A}{P_B} \quad (3)$$

enables both τ_A and τ_B to be obtained.

Equation 1 is applicable in the temperature range -90°C to -70°C . It proved convenient to use this temperature range for determining the dependence of the ligand exchange process on the concentrations of complex and of free ligand since the ability to observe the changes in line width of both resonances independently gives direct mechanistic information. Equation 2 is applicable in the temperature range -30°C to $+10^\circ\text{C}$. Below -30°C the exchange broadening is too excessive for accurate measurements. Above $+10^\circ\text{C}$ the effects of additional line broadening due to the onset of free rotation about the C-N bond of the uncomplexed ligand become significant. Thus -30°C to $+10^\circ\text{C}$ is the preferred temperature range for quantitative line broadening measurements since both the quality of the

spectra in terms of signal to noise ratio and the accuracy of the temperature control are superior to those in the -70°C to -90°C region. The strategy is therefore to obtain qualitative mechanistic data at low temperatures and quantitative rate data in the high temperature region.

There remains the problem of obtaining values of T_{2A} and T_{2B} for use in equation 2. We may obtain values of these relaxation times directly from the line widths at the extreme low temperature end of the measurements where the ligand exchange is too slow to affect the line widths. There is still the question though as to how these line widths vary with temperature. This problem is not too serious for the free ligand line widths T_{2B} since the range of free ligand line widths is relatively small compared with the line widths for the ligand exchange situation and they can in any event be obtained by direct measurements on thiourea solutions over the temperature range in question. The values for complexed ligand T_{2A} present more of a problem. Theoretically the situation is rather complicated. Some previous investigators^{5,6} have assumed that the line widths of complexed ligands will decrease with increasing temperature according to the relationship:

$$\log \Delta\nu_{1/2} \propto \frac{1}{T} \quad (4)$$

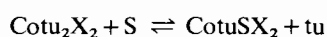
Such a relationship will hold if the line width depends on the rotational correlation time of the molecules in solution which is the case for most relaxation processes. However, for cobalt(II) complexes it has been shown that T_2 is determined by the electron spin relaxation time (T_{1e}) of the metal rather than by molecular tumbling.⁷ T_{1e} may however itself depend on the correlation time for tumbling in solution. Specifically for tetrahedral Co(II) LaMar⁷ has shown that the electron spin relaxation time is determined by coupling of the zero-field splitting with the molecular motion according to the equations:

$$\frac{1}{T_{1e}} = \frac{32\pi^2}{5} \left(\frac{D^2}{h^2} \right) \left[\frac{\tau}{1 + \omega_s^2 \tau^2} + \frac{\tau}{1 + 4\omega_s^2 \tau^2} \right]$$

In this equation D is the usual zero field splitting parameter, τ is the molecular tumbling time and ω_s is the Larmor frequency in radians per sec for the electron spin measured at the magnetic field used in the NMR experiment. Obviously if $\omega_s^2 \tau^2 \gg 1$ $\frac{1}{T_{1e}} \propto \frac{1}{\tau}$ and if $\omega_s^2 \tau^2 \ll 1$ $\frac{1}{T_{1e}} \propto \tau$. Since the nuclear spin relaxation time becomes shorter as the electron spin relaxation time becomes longer and τ becomes smaller with increasing temperature, in the first case the NMR line should become narrower with increasing temperature and in the second case it should become broader. LaMar estimated $\omega_s^2 \tau^2 = 20$ for a specific case but this value is sufficiently

close to unity to make the generalization to other cobalt complexes in different solvents somewhat hazardous. Indeed, Frankel⁸ has found that for solutions of Co^{2+} in water $\frac{1}{T_2}$ for the protons is virtually independent of viscosity implying no dependence on rotational correlation time and Zumdahl and Drago⁵ have reached a similar conclusion with regard to the ligand protons of Cobalt hexamethylphosphoramide complexes. In this laboratory we have observed that the line widths of some β diketone complexes of Vanadium(III) vary very little over a wide range of temperatures. The relaxation situation for these octahedral Vanadium(III) complexes should be quite similar to that for tetrahedral Co(II). For measurements involving the NH_2 protons of thiourea there is an additional complication in that relaxation processes arising from interaction with the quadrupole moment of the nitrogen can also contribute to the line width. Transition from a sharp singlet at low temperatures to a broad singlet at higher temperatures and eventually to a resolved triplet is expected.⁹

In the light of the above discussion it did not seem desirable to obtain the line widths of the complexed thiourea by extrapolation from higher or lower temperatures as has been done by previous investigators. Neither is it possible to obtain this data by direct measurement of the thiourea line widths of solutions to which no excess thiourea ligand has been added since the dissociative equilibrium:

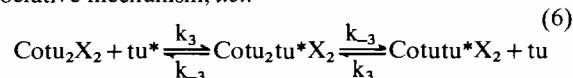


(S = solvent acetone) has been demonstrated. Equilibrium constants for this reaction are however relatively small and the chemical shifts of complexed thiourea have been obtained by plotting observed shifts against $1/\sqrt{c}$ where c is the concentration of cobalt complex. When $1/\sqrt{c} = 0$ the concentration of free ligand is zero and equation 2 indicates that $\frac{1}{T_2'} = \frac{1}{T_{2A}}$. The line widths for complexed thiourea can therefore be obtained by plotting the observed line widths for solutions without added excess thiourea against $1/\sqrt{c}$ and extrapolating to $1/\sqrt{c} = 0$. Essentially therefore we have replaced the temperature extrapolation used by previous investigators to obtain the limiting line widths with a concentration extrapolation and regard this as the more reliable method since it is based on an experimentally established equilibrium rather than a theoretical consideration regarding the relaxation mechanism.

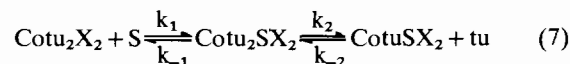
Ligand Exchange Kinetics

Analysis of the NMR data gives the lifetimes τ_A and τ_B for complexed and free ligand molecules. These

parameters must be related to the rates of specific reactions. From qualitative measurements in the slow exchange (low temperature) region it was previously demonstrated that two mechanisms must be considered.² The first of these is direct exchange by an associative mechanism, *i.e.*:



The second is exchange via a solvated intermediate, *i.e.*



Since there is no evidence for any experimentally measurable concentrations of five-coordinate complexes it is assumed in both cases that the overall rate of ligand exchange is determined by the rate of formation of the five-coordinate intermediate. On this assumption we find:

$$\frac{1}{\tau_A} = k_1[\text{s}] + k_3[\text{tu}] \quad (8)$$

and

$$\frac{1}{\tau_B} = [\text{Cot}_2\text{X}_2] \left[\frac{Kk_2[\text{s}]}{[\text{tu}]} + k_3 \right] \quad (9)$$

where k_1 , k_2 and k_3 are second order rate constants and K is the equilibrium constant for the overall reaction 7. k_1 and k_3 may therefore be obtained from the intercept and slope respectively of a plot of $1/\tau_A$ versus $[\text{tu}]$. From equation 9 k_2 and k_3 are obtained as the slope and intercept of a plot of $1/\tau_B$ versus $[\text{Cot}_2\text{X}_2]/[\text{tu}]$. The equilibrium constant K is known from previous results. The two values of k_3 obtained by this analysis provide an indication of the likely systematic errors in experiments of this type. Free energies of activation may be calculated for each of the reactions from:

$$k = \frac{kT}{h} e^{\frac{-\Delta G^\ddagger}{RT}}$$

Enthalpies and entropies of activation are then obtained by plotting ΔG^\ddagger against temperature.

Results

Measurements have been made on eight complexes of the type CoL_2X_2 in which L = thiourea, N-methylthiourea and N,N'-dimethylthiourea and X = Cl, Br, I. Limited solubility in acetone prevented us from obtaining data for the compound with L = N,N'-dimethylthiourea and X = Cl. In each case the primary data collected comprised a set of line widths and line positions obtained for seven concentrations of metal complex to each of which was added free ligand at five different concentrations. Measurements were carried out over the temperature range -30°C to $+10^\circ\text{C}$.

For the thiourea complexes measurements were made on the low field (-1000 to -2000 Hz from TMS at 60 MHz) line associated with the "inside NH" proton. For the methyl and dimethyl ligands the lower field CH_3 resonance was used.

The data was analysed using equation 2. As indicated above $1/T_{2A}$ was found by extrapolating the line width to $1/\sqrt{c} = 0$ at each temperature. Several of these plots are shown in Figure 1. We note that the NH line width decreases from approximately 100 Hz at -20°C to 60 Hz at $+10^\circ\text{C}$. The width of the complexed thiourea at -80°C is 100 Hz. On the other hand above 10°C the limiting line width again increases. It is obvious that the temperature dependence is by no means simple exponential. Over the -30°C to $+10^\circ\text{C}$ temperature range the widths of the CH_3 resonances are in the range 20–40 Hz. Free ligand

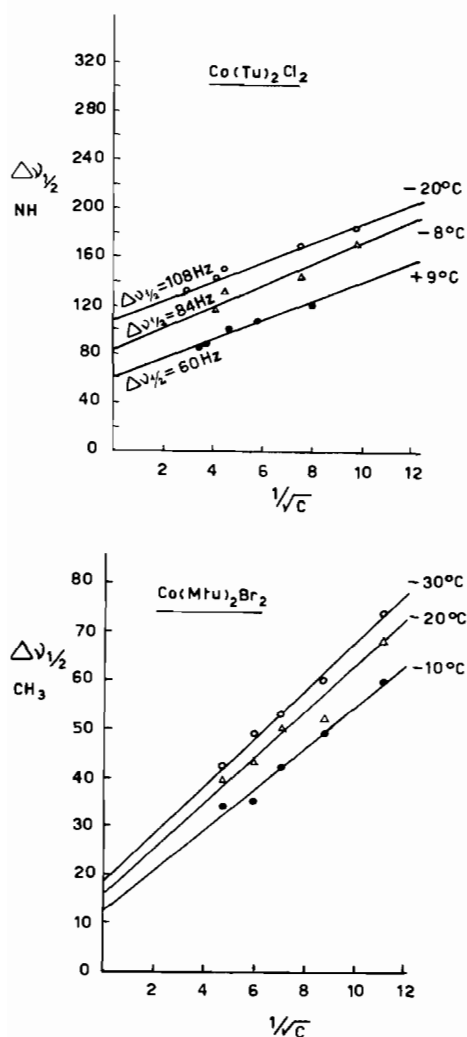


Figure 1. Concentration dependence of the NMR line widths of Co(II) Thiourea Complexes.

line widths were measured directly at the different temperatures and vary from 20 Hz to 40 Hz. It may be noted that the experimental line widths $1/T_{2'}$ vary from 200–400 Hz for the NH and from 100–200 Hz for the CH_3 resonances. The $1/T_{2A}$ and $1/T_{2B}$ terms in equation 2 therefore contribute between 10% and 50% of the total width depending on temperature and concentration.

The chemical shifts of the complexed ligands and of the free ligands are known. We may therefore calculate the fraction of ligand complexed P_A and the fraction free P_B directly from the observed average shifts. Equations 2 and 3 now give τ_A and τ_B . Typical plots of $1/\tau_A$ and $1/\tau_B$ used to obtain the rate constants k_1 , k_{-2} and k_3 are shown in Figures 2 and 3.

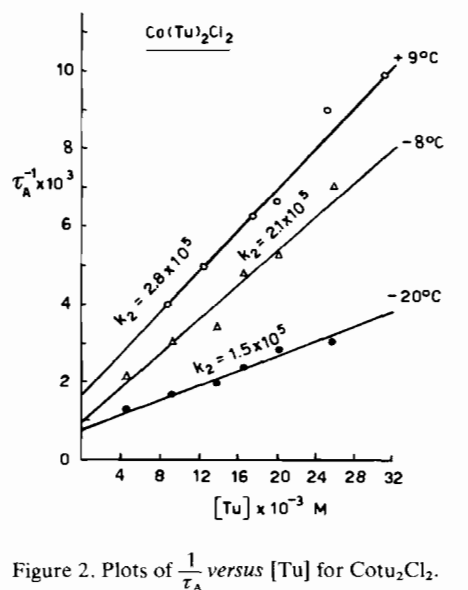


Figure 2. Plots of $\frac{1}{\tau_A}$ versus $[\text{Tu}]$ for CoTu_2Cl_2 .

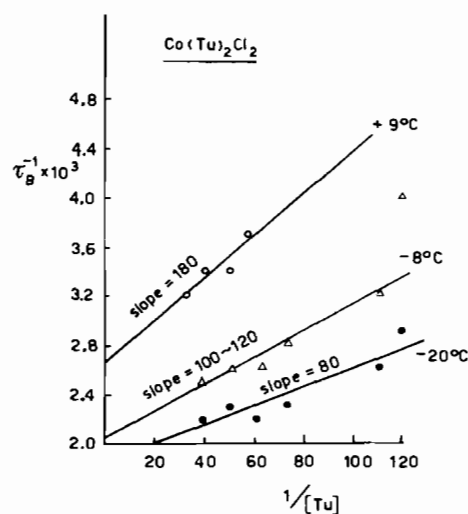


Figure 3. Plots of $\frac{1}{\tau_B}$ versus $\frac{1}{[\text{Tu}]}$ for CoTu_2Cl_2 .

Finally rate constants at room temperature and activation parameters for the three ligand replacement reactions for all eight complexes are gathered together in Table I.

Discussion

The data of Table I shows a number of interesting features. We note first that two term expressions for the rate of substitution of square planar complexes of platinum are quite common.¹ One mechanism involves substitution by a solvent molecule followed by replacement of the solvent by incoming ligand and the second term is a simple bimolecular ligand exchange. This situation is less well documented for tetrahedral Co(II) complexes. The first order term reported for Co(II) hexamethylphosphoramides was considered to represent a dissociation mechanism.⁵ We consider that the "first order" term observed in the present work almost certainly involves prior solvent substitution and this conclusion is strongly supported by the large negative entropy of activation for the process. A dissociative process should lead to a positive entropy of activation and this is indeed found to be the case for octahedral Ni(II) thiourea complexes. The rate constants for this process have accordingly been reported as second order constants to allow direct comparison with the other rate processes.

The three different reactions for which data are available are:

- $\text{CoTu}_2\text{X}_2 + \text{S} \rightarrow \text{CoTu}_2\text{SX}_2 \quad k \sim 10^2 M^{-1} \text{sec}^{-1}$
- $\text{CoTu}_2\text{X}_2 + \text{tu} \rightarrow \text{CoTu}_3\text{X}_2 \quad k \sim 10^5 M^{-1} \text{sec}^{-1}$
- $\text{CoTuSX}_2 + \text{tu} \rightarrow \text{CoTu}_2\text{SX}_2 \quad k \sim 10^7 M^{-1} \text{sec}^{-1}$.

The three reactions have very different rate constants. These rates may be compared with the second order rate constants for square planar platinum compounds¹ (10 – $10^4 M^{-1} \text{sec}^{-1}$) and those for Co(II) hexamethylphosphoramide complexes⁵ ($\sim 10^2$) and Co(II) phosphines ($\sim 10^3$). Since the previous tetrahedral cobalt data refers to analogues of reaction b) it is apparent that the thiourea complexes are the most labile yet studied. We note at this point that the two sets of values for k_3 agree well in order of magnitude and in relative values for different compounds. There is a disagreement of approximately a factor of 2 in absolute magnitude which in all probability reflects systematic errors in the equilibrium constants and line widths used in the calculations.

We turn now to a consideration of the activation parameters. The entropies of activation all fall in the range -20 to -40 e.u. which is very similar to the values found for associative exchange for Pt(II), Pd(II), Ni(II) and Co(II) complexes reported in the literature. The greater lability of the present com-

TABLE I. Kinetic and Activation Parameters for Ligand Exchange Reactions.

Compound	k_1 $M^{-1} \text{sec}^{-1}$	ΔH^\ddagger_1 Kcal mol^{-1}	ΔS^\ddagger_1 e.u.	k_2^a $M^{-1} \text{sec}^{-1}$	ΔH^\ddagger_2 Kcal mol^{-1}	ΔS^\ddagger_2 e.u.	k_3^b $M^{-1} \text{sec}^{-1}$	ΔH^\ddagger_3 Kcal mol^{-1}	ΔS^\ddagger_3 e.u.	ΔH^\ddagger_{-2} Kcal mol^{-1}	ΔS^\ddagger_{-2} e.u.	ΔH Kcal mol^{-1}	ΔS e.u.
Co(Tu) ₂ Cl ₂	1.8×10^2	3.6 ± 0.6	-36 ± 2	3.5×10^5	1.3 ± 0.6	-29 ± 2	3.4×10^7	0.9 ± 0.6	-21 ± 2	0.9 ± 0.6	-21 ± 2	$+3.5 \pm 0.4$	-5.8 ± 1.5
Co(Tu) ₂ Br ₂	1.3×10^2	3.5 ± 0.6	-37 ± 2	2.6×10^5	2.9 ± 0.6	-24 ± 2	2.3×10^7	0.6 ± 0.6	-23 ± 2	0.6 ± 0.6	-23 ± 2	$+4.0 \pm 0.4$	-2.5 ± 1.6
Co(Tu) ₂ I ₂	1.1×10^2	3.4 ± 0.6	-38 ± 2	1.6×10^5	3.2 ± 0.6	-24 ± 2	4.4×10^6	-0.2 ± 0.6	-29 ± 2	-0.2 ± 0.6	-29 ± 2	$+6.1 \pm 0.8$	$+4.9 \pm 2.8$
Co(Mtu) ₂ Cl ₂	1.5×10^2	4.4 ± 0.9	-34 ± 3	2.9×10^5	2.3 ± 0.9	-26 ± 3	2.5×10^7	0.5 ± 0.6	-23 ± 2	0.5 ± 0.6	-23 ± 2	$+3.2 \pm 0.5$	-6.6 ± 2.1
Co(Mtu) ₂ Br ₂	1.2×10^2	4.1 ± 0.9	-35 ± 3	2.3×10^5	3.1 ± 0.6	-25 ± 2	2.4×10^7	0.2 ± 0.6	-26 ± 2	0.2 ± 0.6	-26 ± 2	$+3.9 \pm 0.2$	-4.5 ± 0.9
Co(Mtu) ₂ I ₂	3.7×10^1	4.0 ± 0.6	-38 ± 2	6.1×10^4	3.8 ± 0.6	-23 ± 2	2.2×10^7	0.00 ± 0.6	-25 ± 2	0.00 ± 0.6	-25 ± 2	$+2.3 \pm 0.1$	-8.9 ± 0.5
Co(Dmtu) ₂ Br ₂	4.3×10^1	3.6 ± 0.6	-39 ± 2	8.9×10^4	3.5 ± 0.4	-24 ± 2	1.9×10^7	1.7 ± 0.4	-20 ± 2	1.7 ± 0.4	-20 ± 2	$+2.3 \pm 0.1$	-8.9 ± 0.5
Co(Dmtu) ₂ I ₂	2.5×10^1	3.8 ± 0.6	-40 ± 2	8.5×10^4	4.8 ± 0.6	-20 ± 2	1.7×10^7	0.7 ± 0.4	-24 ± 2	0.7 ± 0.4	-24 ± 2	$+3.3 \pm 0.9$	-5.1 ± 3.6

^a From Equation 8. ^b From Equation 9.

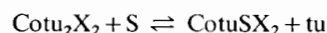
pounds is due very largely to lower enthalpies of activation. We also note that for all series of compounds of Co(II) and Ni(II) of stoichiometry ML_2X_2 the exchange rates fall in the order $Cl > Br > I$. This order has been found for all the CoL_2X_2 series thus far examined. The rationalization originally suggested¹⁰ for the phosphine complexes was that stronger π -bonding resulting from $d\pi$ to $d\pi$ electron donation to the phosphine was to be expected because I^- was a better π -donor than Cl^- . This would lead to greater difficulty in breaking the phosphorus-cobalt bond. Pignolet and Horrocks³ questioned this interpretation since they found the rates depended more on ΔS^\ddagger than ΔH^\ddagger . In the present compound the ΔH^\ddagger values do indeed increase in the right order but since the rate determining step is formation of the five-coordinate complex rather than loss of ligand this earlier interpretation does not appear to be correct. Again in agreement with the phosphine results substitution on the exchanging ligand has relatively little effect on the rates. Exchange is somewhat slower for the methyl substituted thioureas and this is mainly due to larger enthalpy of activation.

Perhaps the most interesting comparison is between the activation parameters for the three reactions a), b) and c). The average enthalpies of activation for the eight examples of each reaction are 3.8 Kcal, 3.1 Kcal and 0.5 Kcal for a, b and c respectively. The corresponding average entropies of activation are -32, -24 and -23 e.u. Reaction of acetone with $Cotu_2X_2$ is slower than reaction of thiourea with $Cotu_2X_2$ largely because of the less favourable entropy of activation. On the other hand reaction of thiourea with $Cotu_2X_2$ is slower than reaction of thiourea with $CotuSX_2$ almost entirely because of the very low (practically zero) enthalpy of activation in the latter case. Thus it seems that the enthalpy of activation for these compounds is predominantly determined by the nature of the metal complex but the entropy is determined by the nature of the incoming ligand.

Some recent results obtained in this laboratory¹¹ have indicated that thiourea is a much stronger second sphere ligand towards the Co(II)-thiourea complexes than is acetone. This result is perhaps not surprising in view of the obvious hydrogen bonding possibilities of thiourea. It is tempting to suggest therefore that substitution by acetone is an essentially associative¹²

(A) process whereas substitution by thiourea involves an interchange¹² (I_A) mechanism. If this is the case the above results indicate that the availability of the I_A mechanism reduces the entropy of activation required, since the incoming ligand is already present in the second coordination sphere, but that the enthalpy of activation is largely determined by the relative bonding abilities of the two ligands involved.

Finally we have also included in Table I the previously reported² values of ΔH and ΔS obtained from the temperature dependence of the equilibrium constant of the reaction:



It is interesting that the values of ΔH are quite similar to those of ΔH^\ddagger for the same reactants. The values of ΔS on the other hand are quite small and may be either positive or negative whereas the ΔS^\ddagger 's are all large and negative. Thus almost the entire activation barrier arises from the entropy term, *i.e.*, the enthalpy of the transition state is virtually the same as that of the product. This observation is of course consistent with the very small ΔH^\ddagger 's observed for the reverse reaction c).

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