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Kinetic Studies of Ring Closures in Platinum(II) Chelates. Rate Constants and Activation Parameters for Chelation of Platinum(II) by Bis(2-aminoethyl) Sulfide in Aqueous Solution

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The complexes $[PtCl_3(basH_2)]^+$ and $[PtCl_2(basH)]^+$ (bas = bis(2-aminoethyl) sulfide) have been prepared, and the kinetics of Pt–bas ring closures have been studied. In basic media the rate constants for closure of the first and second chelate rings are 3.6 ± 0.2 and 0.173 ± 0.005 s^{-1} ($\mu = 0.4$ M, 25 °C), respectively. Corresponding activation parameters are $\Delta H^{\ddagger} = 14.2 \pm 0.3$ kcal/mol and $\Delta S^{\ddagger} = -8.2 \pm 0.8$ cal/(deg mol) (first ring) and $\Delta H^{\ddagger} = 15.7 \pm 0.1$ kcal/mol and $\Delta S^{\ddagger} = -9.0 \pm 0.5$ cal/(deg mol) (second ring). The results when compared with data obtained for ring closures in tridentate nitrogen-donor Pt(II) chelates suggest that ring strain is involved in reaching the transition states, with the second closure involving more strain than the first.

Introduction

Four-coordinate, planar complexes of platinum(II) containing polydentate amine ligands have been studied extensively.[1] Very little is known, however, about the activation energetics associated with closure of the two rings in the formation of a tridentate chelate of Pt(II). For this reason, we have synthesized the complexes $[PtCl_3(basH_2)]^+$ and $[PtCl_2(basH)]^+$ (bas = bis(2-aminoethyl) sulfide) and have investigated the kinetics of the ring-closure reactions. This study has allowed a comparison of the kinetic data with similar results previously reported on the closure of the first[2] and of the second rings[2,3] in *trans*-$[PtCl_2(enH)_2]^{2+}$ (enH = monoprotonated ethylenediamine) and $[PtCl_2(bama)\cdot HCl)]$ (bama = bis(2-aminoethyl)methylamine). Information on the influence of the nature of the central atom of the bas ligand on the ring-closure rates has thus been obtained.

Experimental Section

Materials. Commercial reagent grade chemicals were used without further purification. K_2PtCl_4 was obtained from Johnson-Matthey and bis(2-aminoethyl) sulfide(bas) was prepared by the method of Smolin and co-workers[4] or by the alkaline hydrolysis of diphthalimidodiethyl sulfide.[5]

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Measurements. Conductivities of 10^{-3} M solutions of Pt(II) complexes in dimethyl sulfoxide or water were measured at 25 °C by using a Halosis bridge. Infrared spectra of KBr pellets and Nujol mulls were recorded on a Perkin-Elmer 457 spectrophotometer.

Synthesis of Complexes. [Bis(2-aminoethyl) sulfide)]trichloroplatinum(II) Chloride, [PtCl₃(basH₂)]Cl. To a stirred solution of 1.2 g (10 mmol) of $S(CH_2CH_2NH_2)_2$ in 50 mL of 2 M HCl at room temperature was added at ca. 0.2 mL/min an aqueous solution (50 mL) of 4.15 g (10 mmol) of K_2PtCl_4. The resulting orange solution was concentrated to 20–25 mL and cooled at 5 °C. The KCl precipitated at this stage was removed by suction filtration. By further concentration of the solution, orange crystals of $[PtCl_3(basH_2)]Cl$ were obtained. These were recrystallized from 2 M HCl. The yield was ca. 60%. Anal. Calcd: C, 10.46; H, 3.07; N, 6.10; Cl, 30.88. Found: C, 10.10; H, 3.14; N, 5.80; Cl, 30.39. Mp (uncor) 222 °C.

[Bis(2-aminoethyl) sulfide hydrochloride]dichloroplatinum(II), [PtCl₂(bas·HCl)]. This complex was obtained under the same experimental conditions as in the previous preparation, except that the pH was kept in the range 1–2. The resulting yellow-orange solution was concentrated to 20–25 mL and cooled, whereupon white crystals of KCl separated out. The $[PtCl_3(basH_2)]Cl$ and $[PtCl_2(bas·HCl)]$ complexes, which are both present in the final solution, were separated by fractional crystallization. The yellow compound $[PtCl_2(bas·HCl)]$, which was precipitated initially, was recrystallized from 1 M HCl (5 mL) (yield 40%). These complexes were also prepared in a different way by Mann[6] but were not characterized completely. Anal. Calcd: C, 11.37; H, 3.10; N, 6.63; Cl, 25.16. Found: C, 11.06; H, 3.42; N,

6.33; Cl, 25.44. Mp (uncor) 103 °C; Λ_m(Me$_2$SO) 41.2.

[Bis(2-aminoethyl) sulfide]chloroplatinum(II) Chloride, {[PtCl-(bas)]Cl}$_n$. An aqueous solution containing 0.84 g (2 mmol) of [PtCl$_2$(bas·HCl)] was added dropwise to 2 mL of 1 M NaOH. The yellow-white product separated after standing overnight at room temperature and was recrystallized from hot water. The yield was >80%. Anal. Calcd: C, 12.44; H, 3.13; N, 7.26; Cl, 18.36. Found: C, 12.12; H, 3.19; N, 7.00; Cl, 18.25. Mp (uncor) 231 °C; Λ_m(H$_2$O) 128.2.

Kinetics. Rate data in acidic solution were obtained with an Optica CF4R double-beam instrument. Acetate buffer (0.4 M) was used to control the pH of reaction mixtures. Solutions for kinetic experiments on the [PtCl$_3$(basH$_2$)]Cl complex were prepared by adding a solution containing the buffer to a weighed amount of solid compound. The solutions were brought to the reaction temperature before adding the complex. In the case of [PtCl$_2$(bas·HCl)], separate aqueous solutions of 0.4 M acetic acid containing the reacting complex and of 0.4 M sodium acetate were brought to the reaction temperature and then mixed (to attain the required pH) and placed in the thermostated cell of the spectrophotometer. All the reactions studied were found to follow first-order kinetics, and the rate constants were calculated from plots of $-\log (A_\infty - A_t)$ against time. The rates of reaction in basic solutions were obtained with a Durrum D-110 stopped-flow instrument.

Results

By addition of an aqueous solution of K$_2$PtCl$_4$ dropwise to bis(2-aminoethyl) sulfide in acidic media with pH <0 at room temperature, the [PtCl$_3$(basH$_2$)]$^+$ complex formed. If a solution of the ligand was added to a solution of the platinum salt, a red-brown oil formed, which with stirring dissolved in 1 day giving a solution of the final complex. The oily product crystallized by standing or by dissolution in warm water, but its very poor solubility prevented proper characterization. The analytical data obtained[7] accord with the formula [PtCl$_3$-(basH$_2$)]$_2$PtCl$_4$. The [PtCl$_2$(basH)]$^+$ cation was similarly obtained by reacting K$_2$PtCl$_4$ with the ligand in a solution at pH 1–2. The [PtCl$_3$(basH$_2$)]$^+$ complex that simultaneously formed was separated by fractional crystallization. Since both products have about the same solubility as KCl, the use of Li$_2$PtCl$_4$ facilitated purification.

The conductance values for [PtCl$_2$(bas·HCl)] and {[PtCl(bas)]Cl}$_n$ are in agreement with those for 1:1 electrolytes.[8] The IR spectra of [PtCl$_3$(basH$_2$)]$^+$ and [PtCl$_2$-(basH)]$^+$ exhibit bands attributable to the presence of protonated amine groups.[7] These bands are not observed[7] for the {[PtCl(bas)]Cl}$_n$ complex, which has only coordinated amine functions. In the Pt–Cl stretching region, only a band at 330 cm^{-1} is observed for the {[PtCl(bas)]Cl}$_n$ compound, whereas there are two absorption bands for [PtCl$_2$(bas·HCl)] (328 and 300 cm^{-1}) and for [PtCl$_3$(basH$_2$)]$^+$ (333 and 301 cm^{-1}). Similar values have been found (343–326 cm^{-1} and 314–305 cm^{-1}) for K[PtCl$_3$L] (L = monodentate neutral ligand) compounds.[9]

The unchelated [PtCl$_3$(basH$_2$)]Cl complex is stable in very acidic solutions (pH <1), but at lower acidities a two-step reaction takes place with formation first of the [PtCl$_2$(basH)]$^+$ cation and then of the complex in which both rings are closed. The spectroscopic changes observed in this reaction are shown in Figure 1. Two well-defined isosbestic points at 269 and 325 nm are associated with the closure of the first ring. At this point, the spectrum of the product of the reaction corresponds to that of a sample of [PtCl$_2$(bas·HCl)], which was prepared independently. This complex is unstable at pH >1, as at these higher pH values the second ring closes to form the final product. Kinetic studies on the closure of the second ring were performed by using the [PtCl$_2$(bas·HCl)] complex as starting material. Three isosbestic points are observed, at 246, 280, and 318 nm (Figure 2). The main feature of the spectrum of the final reaction product is a maximum at 258 nm (ϵ 390), which is very similar to maxima observed in the
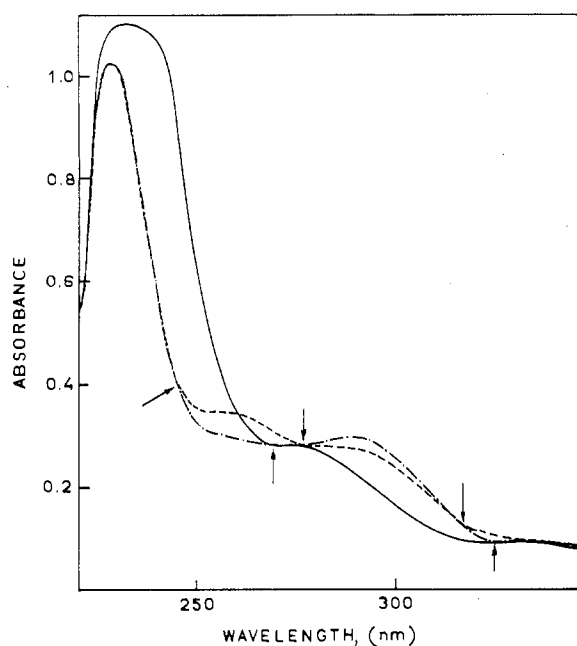

Figure 1. Spectra in 0.4 M acetate buffer solution of [PtCl$_3$(basH$_2$)]Cl (—) (initial concentration 1.0×10^{-3} M) and the two reaction products (–·– and - - -) at 25 °C. The arrows indicate the isosbestic points observed at 246, 269, 280, 318, and 325 nm.
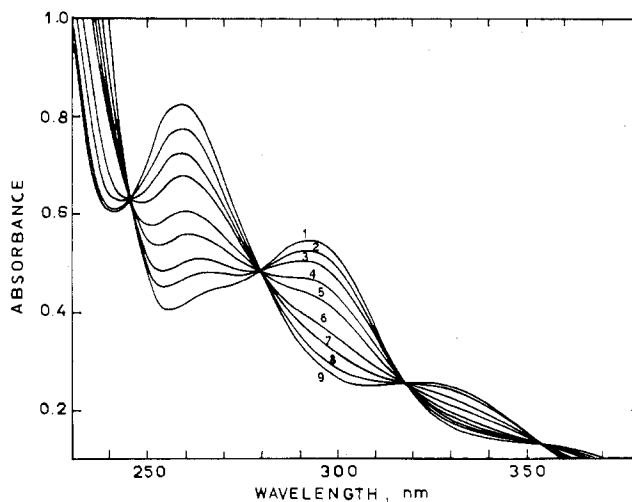

Figure 2. Spectral changes associated with closure of the second five-membered Pt–bas ring at 25 °C ([[PtCl$_2$(bas·HCl)]] = 2.1×10^{-3} M; [H$^+$] = 7.1×10^{-6} M; μ = 0.4 M). Curves 1–9 show, respectively, spectra at zero time and after 10, 20, 40, 61, 105, 150, 240, and 420 min.

spectra of [PtCl(dien)]$^+$ [dien = bis(2-aminoethyl)amine] (λ_{max} 260 nm) and [PtCl(bama)]$^+$ [bama = bis(2-amino-ethyl)methylamine] (λ_{max} 258 nm).[3] On this basis it is reasonable to propose that the product of the second reaction step is a monomeric platinum(II) derivative in which both amine groups of bas are coordinated to the metal.[10]

The k_{obsd} for the first ring closure was calculated from data obtained at 246 nm, where the extinction coefficients of [PtCl$_2$(basH)]$^+$ and the final reaction product are the same (Figure 1). The initial concentration of [PtCl$_3$(basH$_2$)]$^+$ was 1×10^{-3} M, whereas for the second step the concentration of [PtCl$_2$(basH)]$^+$ used was 2×10^{-3} M. The rate constants[11] for both steps of the reaction are linear functions of the reciprocal of the hydrogen ion concentration, according to eq 1. The values of the parameters B_0 and B_1 at different

$$k_{obsd} = B_0 + B_1/[\text{H}^+] \tag{1}$$

Table I. B_1 and B_0 Values and B_1 Activation Parameters

complex	temp, °C	$10^9 B_1$, M s^{-1}	$\Delta H^{\ddagger}$, kcal/ mol	$\Delta S^{\ddagger}$, cal/(deg mol)	$10^5 B_0$, s^{-1}
[PtCl$_3$-(basH$_2$)]Cl	19.4	15.2 ± 0.4	17.7± 0.1	−34.0 ± 0.5	
	25.2	21.7 ± 0.7			36 ± 3
	33.0	70 ± 1			29 ± 6
	40.0	104 ± 5			210 ± 20
[PtCl$_2$-(bas·HCl)]	20.0	0.62 ± 0.01	20.9 ± 0.1	−29.4 ± 0.4	0.8 ± 0.2
	25.0	1.03 ± 0.04			1.2 ± 0.6
	33.0	3.00 ± 0.08			8 ± 1
	40.0	6.1 ± 0.3			21 ± 3

Table II. Kinetic Parameters for Ring-Closure Reactions Measured in Basic Media at 25 °C ($\mu = 0.4$ M)

complex	$\Delta H^{\ddagger}$, kcal/mol	$\Delta S^{\ddagger}$, cal/ (deg mol)
[PtCl$_3$(bas)]$^-$ (C)	14.2 ± 0.3	−8.2 ± 0.8
$k_1' = 3.6 \pm 0.2$ s^{-1}		
$k_1 K_{a_1} = (21.7 \pm 0.7) \times 10^{-9}$ M s^{-1}		
[PtCl$_2$(bas)] (E)	15.7 ± 0.1	−9.0 ±0.5
$k_2 = 0.173 \pm 0.005$ s^{-1}		
$K_{a_2} = (5.9 \pm 0.4) \times 10^{-9}$ M		

temperatures are given in Table I. Parameter values were obtained by least-squares analyses of plots of k_{obsd} vs. $1/[\text{H}^+]$. Activation parameters based on B_1 values (Table I) were calculated by using an unweighted least-squares procedure. The rates of the ring-closure reactions in basic media were obtained by a stopped-flow technique in which a 0.4 M NaClO$_4$ solution containing 0.001 M HClO$_4$ and [PtCl$_3$-(basH$_2$)]$^+$ or the [PtCl$_2$(basH)]$^+$ complex was mixed with a 0.4 M NaClO$_4$ solution containing NaOH to bring the pH of the reaction mixture above 11. Results are set out in Table II.

Discussion

In acidic media, the observed rate constants for the closure of the first and second rings of [PtCl$_3$(basH$_2$)]Cl show an inverse dependence on hydrogen ion concentration. This reciprocal [H$^+$] dependence was anticipated, as deprotonation of a ligand nitrogen is required before bond formation with platinum can occur. Thus in Scheme I, the ring-closure steps are preceded by rapid acid–base equilibria. The first ring-closed products result from acid–base equilibira 1 and 2, forming the intermediates [PtCl$_3$(basH)] (B) and [PtCl$_3$(bas)]$^-$ (C); these intermediates then undergo chelation reactions 3 and 4. The second ring closure involves acid–base equilibrium 5 followed by chelation reaction 6. The derived experimental rate laws for the two steps are

$$k_{obsd} = \frac{K_{a1} K_{a1}' k_1' + K_{a1} k_1 [\text{H}^+]}{K_{a1} K_{a1}' + K_{a1} [\text{H}^+] + [\text{H}^+]^2}$$
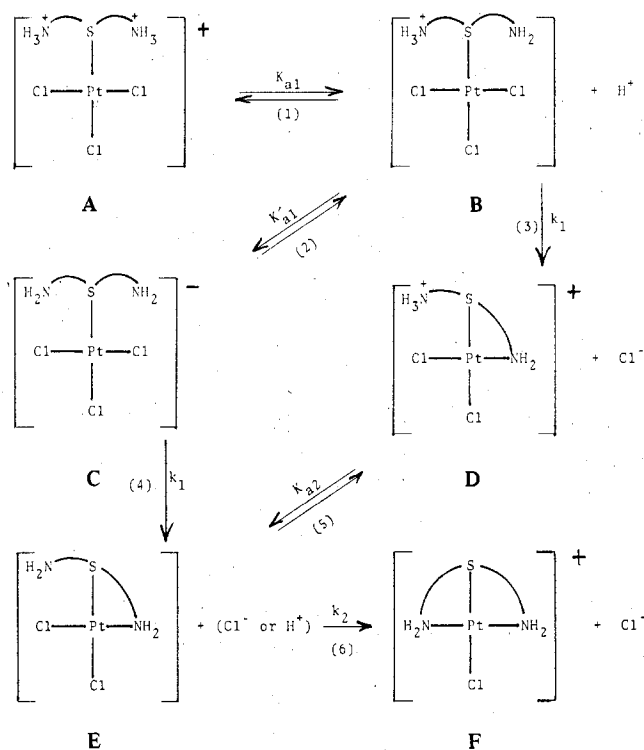
$$k_{obsd} = K_{a2} k_2 / (K_{a2} + [\text{H}^+])$$

On the assumption that in acidic media K_{a1}, K_{a1}', and K_{a2} are much smaller than [H$^+$], the expressions for the rate constants reduce to

$$k_{obsd} = K_{a1} k_1 / [\text{H}^+]$$

$$k_{obsd} = K_{a2} k_2 / [\text{H}^+]$$

The B_1 terms, which are the slopes of the plots k_{obsd} vs. [H$^+$]$^{-1}$,

Scheme I

are equal to $K_{a1} k_1$ and $K_{a2} k_2$, respectively. The B_0 terms (the nonzero intercepts), which are analogous to those found for the ring closures of [PtCl(en)(en·HCl)]$^+$, [PtCl$_2$(bama·HCl)], and [PtCl$_2$(taa·2HCl)], are attributable to the usual solvent path.[2,3] In our case, the contribution of the B_0 path to the total rate is small compared to that of the B_1 term and therefore can be neglected. In basic media, pH >11, rapid deprotonations of the uncoordinated amine groups take place, and, as the reaction rate is no longer dependent on the acid-dissociation constant ([H$^+$] << K_{a1}, K_{a1}', and K_{a2}), the values of k_1' and k_2 are directly measured. The rate constant for the closure of the first ring of [PtCl$_3$(bas)]$^-$ is 3.6 ± 0.2 s^{-1} at 25 °C, whereas for the second ring the k_2 value is 0.173 ± 0.005 s^{-1}. The K_{a1} value cannot be derived from the B_1 term of the first step because k_1 is unknown in acidic media. On the other hand, from the B_1 term of the second step, the acid dissociation constant K_{a2} of the [PtCl$_2$(bas·HCl)] complex is obtained as $(5.9 \pm 0.4) \times 10^{-9}$ M. This K_{a2} value can be compared with the first and second ionization constants (1.44 × 10^{-9} and 2.26 × 10^{-10} M) of the free ligand, S(CH$_2$CH$_2$NH$_3^+$)$_2$.[12] It is apparent that coordination at two sites of the tridentate ligand makes the remaining protonated amine group a stronger acid than both amine functions in the free ligand. Similar results were obtained[2,3] for the [PtCl$_2$(bama·HCl)] and *trans*-[PtCl$_2$(enH)$_2$]$^{2+}$ complexes.

The rate constant for closure of the first ring in the [PtCl$_3$(bas)]$^-$ complex (3.6 ± 0.2 s^{-1}) is smaller than the corresponding value (10.4 ± 0.6 s^{-1}) obtained for *trans*-[PtCl$_2$(en')$_2$] (en' = monodentate ethylenediamine) (Table II). As both complexes have the same labilizing group trans to the leaving Cl$^-$, the different rates may be explained in terms of the different total charge and/or the different cis influence of the sulfur atom on the leaving group in our case, as compared with the cis effect of the nitrogen atom in the en' complex. An examination of the literature data does not allow a simple decision as to which of these two effects is more important, although it is known that charge and cis effects as well as proton basicities have little influence on the rate of substitution in platinum(II) complexes.[13,14] Thus the possible ring strain due to the larger radius of the sulfur atom as

Table III. Ring-Closure Rate Constants and Acid Dissociation Constants at 25 °C for Some Platinum(II) Complexes

complex	μ, M	k, s^{-1}	K_a, M	ref
trans-[PtCl$_2$-(en')(en')]	1.0	10.4 ± 0.6	(1.2 ± 0.1) × 10^{-8}	2
[PtCl-(en')en]$^+$	1.0	0.73 ± 0.006	(1.1 ± 0.1) × 10^{-8}	2
[PtCl$_2$-(bama)]	0.4	2.1 ± 0.1	(2.5 ± 0.3) × 10^{-9}	3
[PtCl$_2$-(taa)]^a	0.4	4.3 ± 0.2		3
[PtCl$_3$-(bas)]$^-$	0.4	3.6 ± 0.2		this work
[PtCl$_2$-(bas)]	0.4	0.173 ± 0.005	(5.9 ± 0.4) × 10^{-9}	this work

^{a} taa = tris(2-aminoethyl)amine.

compared to that of the nitrogen may make a significant contribution.

The rate constant for the second ring closure is 0.173 ± 0.005 s^{-1}, which can be compared with the values of 2.1 ± 0.1 s^{-1} and 4.3 ± 0.2 s^{-1}, respectively, obtained for [PtCl$_2$(bama)] and [PtCl$_2$(taa)] (Table III). The difference between these latter rates has been attributed to a statistical factor, since the taa complex has two equivalent amine groups available for coordination, whereas the bama complex has only one. Examination of data from crystal structure analyses suggests that the lower rate constant for the bas complex compared to that of the bama derivative is probably due to very severe steric strain associated with the closure of the second ring. We cite, for example, the fact that the [PtBr(dien)]$^+$ cation has two normal Pt–N bond lengths (1.98 and 1.96 Å), but the third Pt–N (associated with a primary amine group) is 2.12 Å,[15] indicating that one five-membered ring is strained. Such strain would be exacerbated in a Pt(II) chelate containing bas, since Pt–S bond lengths are about 2.25 Å.[1,16] The Pt–bas ring closure activation entropies in basic media (Table II) (−8.2

± 0.8 and −9.0 ± 0.5 cal/(deg mol)) are more positive than those usually found for bimolecular substitution processes in Pt(II) complexes (−14 to −30 cal/(deg mol)),[17] consistent with an intramolecular mechanism. Both the $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ values are less favorable for the second ring closure, which accords with the proposal that more strain is involved in reaching the transition state in this final step.

Registry No. [PtCl$_3$(basH$_2$)]Cl, 69551-36-6; [PtCl$_2$(bas·HCl)], 69551-37-7; [PtCl(bas)]Cl, 69551-38-8; [PtCl$_3$(bas)]$^-$, 69551-39-9; [PtCl$_2$(bas)], 69551-40-2.

Supplementary Material Available: Listing of k_{obsd} values for the ring closure reactions (2 pages). Ordering information is given on any current masthead page.

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Kinetic Studies on Four-Coordinate Chelate Complexes of Copper(II): Isotopic Ligand Exchange of Bis(salicylaldiminato)copper(II) in Toluene

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Isotopic exchange technique has been used to study the rate of ligand exchange of a series of ^{131}I-labeled bis(*N*-R-salicylaldiminato)copper(II) complexes (R = ethyl, *n*-propyl, isopropyl, isobutyl, *tert*-butyl, neopentyl) in toluene as a function of the nature of R and properties of substituents X at the salicylaldehyde ring. The rate of exchange follows a two-term rate law, namely, $r_{ex} = (k_S + k_{ligand}[ligand])[complex]$. The occurrence of k_S is found to be due to residual water in toluene, according to $k_S = k_{H_2O}[H_2O]$. The equilibrium constants K(py) for the addition of pyridine to the complexes studied have been measured spectrophotometrically. From the variation of k_S, k_{ligand}, $\Delta H^{\ddagger}(k_S)$, $\Delta H^{\ddagger}(k_{ligand})$, $\Delta S^{\ddagger}(k_S)$, $\Delta S^{\ddagger}(k_{ligand})$, and K(py) with R and X, it is concluded that both the solvent and the ligand term in the observed rate equation can be explained by an associative mode of activation.

Introduction

In recent years only very few kinetic studies based on isotopic exchange experiments have been reported.[1] For most of the kinetic investigations, techniques have been applied which allow on-line measurements.

Isotopic exchange experiments are restricted to slowly exchanging systems because of necessary separation of the exchange partners, and radioisotopes with appropriate half-lives and facile detectability must be available. Apart from these experimental limitations, isotopic exchange experiments

possess some very striking advantages: (i) there is no driving force due to free energy changes, and (ii) the exchange reactions are of high symmetry. This latter aspect means that the derivation of the rate law for an isotopic ligand-exchange reaction of a bis complex, for example, can be restricted to considering only half of the reaction as compared to the nonisotopic case. With complexes containing more than two identical ligands, an even greater simplification is possible.

To our knowledge the ligand exchange of copper(II) salicylaldimines (I) has not yet been investigated kinetically. As