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Reactivity of a Five-Coordinate Complex: Kinetics of Dissociation of [tris(2-dimethylaminoethyl)amine-NN'N"N'''] Cobalt(II) in Solvents and Aqueous Solvent Mixtures

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The kinetics of the dissociation of the five-coordinate complex [tris(2-dimethylaminoethyl)amine-NN'-N"N'''] cobalt(II) in solutions of chloroacetic acid have been studied using stopped-flow spectrophotometry. Solvents used were dimethylformamide, aqueous dimethylformamide, dimethyl sulfoxide, aqueous dimethyl sulfoxide, and acetonitrile. The rate of reaction of the principal step in the dissociation path is proportional to the complex concentration; the first order rate constants in 1.0 mol dm^{-3} chloroacetic acid in the presence of 1.0 mol dm^{-3} sodium perchlorate at 298 K are 18.4, 4.49, 4.05, and 2.40 sec^{-1} in dimethylformamide, dimethyl sulfoxide, acetonitrile, and water, respectively. The reaction rate profiles as a function of water concentration in aqueous dimethylformamide and aqueous dimethyl sulfoxide are similar; a broad maximum rate is observed in the 2–10% water range at 298 K. A consistent trend is found for dissociation of the complex in aqueous dimethylformamide solutions of 1.0 mol dm^{-3} and 0.25 mol dm^{-3} perchloric acid. A slower step in the dissociation is detectable in nonaqueous solvents but cannot be characterized reliably. These results together with the enthalpies and entropies of activation at 298 K are considered in terms of the possibilities of dissociative and associative reaction pathways.

Introduction

The formation and dissociation kinetics of six-coordinate transition metal complexes in aqueous solution, in other pure solvents, and in aqueous mixtures have been thoroughly studied and the mechanisms are relatively well understood [1]. The characteristic reactivities of analogous five-coordinate transition metal complexes have been less exhaustively studied [2, 3]; there are few examples of such complexes with nitrogen donor ligands [4]. Relative dissociation reactivities and energetics in aqueous acid solution have been determined for complexes of three transition metal ions (Co^{2+}, Ni^{2+}, and Cu^{2+}) with the quadridentate amine ligand tris(2-dimethylaminoethylamine-NN'N"N''' (tda) [5]. The results of these studies could be interpreted in terms of either a dissociative or an associative mode of activation in the overall dissociation mechanism.

A study of the lability of the aqua copper (tda) complex to substitution of coordinated water by small ligands, relative to the lability of the copper complex with the unmethylated ligand, showed the importance of the hydrophobicity/hydrophilicity of the local environment [6].

These complexes are of interest from the standpoint of the reactivity of the five-coordinate state. Since the final product of dissociation in the presence of aqueous acid, is the metal ion in a six-coordinate state, studies of the multistage dissociation may reveal kinetic and activation parameters for both processes.

This paper is a report of kinetic studies of the dissociation of cobalt(II) (tda) in acetonitrile, dimethyl sulfoxide, and dimethylformamide, and in aqueous binary mixtures of these solvents.

Experimental

Materials

Preparation of tda 2,2',2"-triaminoethylamine (tren), Ames Laboratories, N.Y., was hexamethylated by a mixture of methanoic acid and methanal. The product distilled as a clear oily liquid under reduced pressure.

Preparation of complexes. Hydrated cobalt(II) perchlorate, G. Frederick Smith Chemical Co., was

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used to prepare [Co(tda)(ClO_4)](ClO_4) by an established method [4a]. It was recrystallized by dissolving in chloroform (dried over calcium hydride and distilled onto molecular sieves), and using petroleum ether (boiling range 70–90 °C, distilled from calcium hydride) as a cosolvent for crystallization.

Analytical reagent grade monochloroacetic acid (Mallinckrodt Chemical Works, N.Y.) and reagent grade perchloric acid (70–72%, J. T. Baker, N.Y.) were used without further purification. Spectrophotometric grade N,N-dimethylformamide, dimethyl sulfoxide, and acetonitrile (Aldrich Chemical Co.) were used without further purification; reagent grade N,N-dimethylformamide and dimethyl sulfoxide were further purified before use. Reagent grade dimethyl sulfoxide was purified by adding barium oxide; after 24 hours it was distilled under reduced pressure. Reagent grade dimethylformamide was stirred over potassium hydroxide and distilled from barium oxide. While care was taken to prevent incursion of water from the atmosphere, these solvents are not rigorously anhydrous; the procedures involved in using the stopped-flow instrument would render futile efforts to remove all extraneous water from the solvents. Deionized water was used to make up aqueous solutions or aqueous mixtures.

Methods

Reactants and products were characterized using a Cary 14 spectrophotometer. The principal purpose was to verify that complete dissociation takes place under the particular acid and solvent conditions.

Kinetic measuremenents were made using a Durrum–Gibson stopped-flow single beam spectrophotometer with a Kel-F flow path and a 2 cm path length cuvette. Temperature control of the drive syringes, the flow path, and the reaction cuvette was maintained in the range used, 278–308.5 K, with an estimated precision of ±0.1 K by circulating fluid from a Neslab RTE-8 thermostat bath. The output signal from the stopped-flow instrument was treated as reported earlier [7] and the data were processed using a DEC-10 computer. Output signals yielded first-order kinetc plots.

Results and Discussion

The dissociation of Co(II) (tda) in pure solvents has been studied spectrophotometrically using chloroacetic acid, a nonaqueous acid. The complex is stable indefinitely in a solution of each solvent relative to its rate of dissociation in acid solution. As expected from earlier aqueous solution studies, the first order rate constant for the principal observed reaction is essentially independent of the complex concentration in the range 5×10^{-4} to 5×10^{-3} mol dm^{-3}, and the reaction is therefore first order in the concentration of Co(II)(tda). The dependence of the rate of this step on acid concentration is not simple; however, at an acid concentration (1.0 mol dm^{-3}) at which the reaction is conveniently studied (*vide infra*), the observed first order rate constant is essentially acid independent. The dissociation of the complex at 470 nm is characterized by an absorbance decrease representing a large fraction of the total theoretically possible change. This is followed by a step which is slower, but still in the stopped-flow range; however this change is of very small amplitude and cannot be reliably characterized. The second and first steps are sufficiently well separated in time that it is possible to analyze them separately, when the acid concentration is 1.0 mol dm^{-3}. When the acid concentration is lowered (for example, below 0.25 mol dm^{-3}) the reaction rate appears to depend significantly on the acid concentration; the two steps are not separable and kinetic characterization becomes very difficult. Consequently, the detailed acid dependence of the reaction could not be studied. The slower step, if kinetically meaningful, appears to be first order, and it is clearly worthy of further investigation. Higher concentrations of metal complex would yield a signal of increased amplitude; however, solubility considerations and other practical limitations precluded this for our study.

This study focusses on the effect of solvent, solvent mixture, and added electrolyte on the reaction rate. In each case, a constant acid concentration was used. Whenever appropriate in the mixed aqueous solutions, the effect of acid strength on the rate of dissociation was investigated. Perchloric acid and monochloroacetic acid were chosen for these studies.

Kinetic and activation parameters for the reaction in pure solvents are collected in Table I. Results for the dissociation in mixed aqueous solutions in the presence and absence of sodium perchlorate are compiled in Table II.

One aim in studying the effects of solvent and total medium on the kinetics of dissociation of the five-coordinate complex is to separate the overall observed effect into contributions to the initial state and to the transition state [8–10]. Assumptions regarding the nature of the activated complex must be made in order to obtain modelled thermodynamic data for the transition state. Knowledge of thermodynamic properties such as transfer solubilities of the reactants is involved. In addition, a high degree of certainty regarding the reaction mechanism is implied. A suitable set of data is rarely available for such a complete analysis, although the method has been used successfully in a few cases. In this study the analysis is therefore restricted to consideration of how the free energy change between the initial state and the transition state is affected by variation of solvent or medium, in the absence of an

TABLE I. Dissociation of Co(II)(tda)(S) by Chloroacetic Acid at 298 K.

Solvent	k s^{-1} 1.0 mol dm^{-3} $NaClO_4$	No salt	$\Delta H^{\neq}$ [a] kJ mol^{-1}	$\Delta S^{\neq}$ [a] J mol^{-1} deg^{-1}
Water	2.40	3.56	48.1	−73
CH_3CN	4.05			
DMSO	4.49	9.38	50.6	−57
DMF	18.4	16.8	51.0	−50

[a] Activation parameters derived from kinetic data for reactions with no inert salt present.

TABLE II. Dissociation of Co(II)tda(S) at 298 K in Aqueous Mixtures.

Solvent % H_2O	DMF k s^{-1}				DMSO CA 1.0 mol dm^{-3}
	CA[a] 1.0 mol dm^{-3} $NaClO_4$[b]	CA 1.0 mol dm^{-3} no salt	$HClO_4$ 1.0 mol dm^{-3}	$HClO_4$ 0.25 mol dm^{-3}	
0	18.4	16.8	30.7	29.3	9.29
2.5	20.3	27.8	28.1	29.7	18.1
5	17.9	26.7	31.5	23.4	16.7
10	14.9	26.5		15.3	13.5
20	9.12	19.2		12.9	9.52
25	7.80	15.8	12.9	8.95	8.15
35	6.14	11.0			
50	4.37	6.63	4.63	5.73	4.11
75	2.84	4.23	3.02	3.51	
100	~2[c]	3.56	2.08	3.05	3.56

[a] CA: chloroacetic acid. [b] 0.8 mol dm^{-3} $NaClO_4$. [c] Estimated by comparison with data for dissociation in $HClO_4$.

indication that these variations cause a change of mechanism.

The overall dissociation in each solvent proceeds by multiple steps. The initial rapid dissociation step involves the greatest change in absorbance and is therefore thought to correspond to the loss of five coordination, since six-coordinate cobalt(II) species have much smaller relative absorptivities [11]. The absence of large differences in the first order rate constant over the range of solvents and solvent mixtures indicates that the mechanism of dissociation is most likely common under the conditions studied (see Tables I and II). The magnitude of the rate-determining step is not influenced significantly by solvent at the acid concentrations used, and is affected by no more than a factor of two in the two different acids used. A mechanism of dissociation in which the rate-determining step involves the breaking of a bond between a dimethylated nitrogen atom and the cobalt ion would necessarily require a source of protons to protonate the released nitrogen, thus preventing bond reformation. In the case of acids not fully dissociated, the undissociated form could be involved in weakening the cobalt–nitrogen bond by forming a hydrogen bond with the ligand nitrogen. The indefinite stability of the complex in the absence of acid suggests a role for the acid in this regard which may be a solvent dependent function due to differing degrees of solvation of the acid, cobalt complex, and activated complex. The closeness of the values of $\Delta H^{\neq}$ in each solvent (a range from 48 to 52 kJ mol^{-1}, (Table I)) indicates a common bond breakage. The supply of protons in strictly anhydrous solvents with chloroacetic acid as the dissociating agent would be negligible; thus the status of the four coordinate intermediate would not be maintained even temporarily before further dissociation occurs. Because water cannot be rigorously excluded, it is likely that a limited supply of protons is available in 'nonaqueous' medium. The dissociation constant of chloroacetic acid is pK_a = 2.64 at 298 K (1.0 mol dm^{-3} ionic strength) [12]; it will be lower in decreasing amounts of water. However a stoichiometric concentration of 5 × 10^{-4} mol dm^{-3}

is all that is required for protonation of one nitrogen of each complex molecule. Water retained by solvents, even after scrupulous drying and maintenance in anhydrous conditions, can be as high as 1% v/v. It is not known what level extraneous water reaches under the conditions of our experiments. It is interesting that the rate constant for dissociation by chloroacetic acid increases from 16.8 s^{-1} in DMF (Table II), with salt absent, to 27.8 s^{-1} at 2.5% H_2O and remains close to this value up to 10% H_2O. A similar maximum appears in DMSO at 2.5% H_2O with k of 18.1 s^{-1}, an increase from 9.29 s^{-1} in 100% DMSO. These maxima could arise as a consequence of the dual effects of the optimal increase in rate constant with increase in organic cosolvent, observed in all circumstances, and the rate retardation below about 2.5% H_2O caused by an inadequate supply of protons. Such maxima are not observed when perchloric acid is the dissociating agent since even with a solution of '100%' organic solvent, water to the extent of 2–2.5% will be present from the dilution of concentrated perchloric acid (70–72%) in 1.0 mol dm^{-3} acid solutions and to a lesser degree in solutions of 0.25 mol dm^{-3} perchloric acid. If the mechanism suggested is appropriate, DMF and to a lesser degree DMSO are able to effectively lower the energy barrier to bond breakage by facilitating the formation of the activated complex for the incipient four-coordinate intermediate. Except for the small amplitude second step reported above, subsequent unwrapping of the ligand from the cobalt ion appears to be rapid.

The values of $\Delta S^{\neq}$, −73, −57 and −50 J mol^{-1} deg^{-1} at 298 K for H_2O, DMSO and DMF respectively (Table II) would indicate a degree of association of species in forming the activated complex which is in conflict with the mechanism discussed earlier. A possible scheme which would accommodate these entropy of activation data would be one in which the undissociated acid or a proton formed an adduct with the five-coordinate metal complex, a consequence of which could be the distortion of the trigonal bipyramid and the insertion of a second solvent molecule into the coordination sphere (the first solvent molecule having replaced the coordinated anion). This would introduce into the reaction pathway a six-coordinate intermediate; the strain induced by this with the ligand still attached would result in rapid dissociation of the cobalt–nitrogen bonds and the production of a hexasolvated cobalt(II) ion. The relative dissociation rate constants in the four solvents are partially consistent with this. Solvent donicities are 18.0, 14.1, 26.8, and 29.6 for water, acetonitrile, dimethylformamide, and dimethyl sulfoxide respectively [13].

Results reveal that the principal observed step is one in which under most conditions the presence of salt favors the production of the activated complex. This is not a large effect but would suggest the generation of charge in the activated complex compared with the reactants. Water would be expected to be attracted to the added salt. This has a consequence for the water concentration in the vicinity of the reactants in both aqueous solvent mixtures of low water concentration where the effective water concentration could be lowered from the bulk value, and in nonaqueous solvents where a significant fraction of the extraneous water may reside in the immediate environment of the salt component. Therefore, interpretation of the effect of the presence of salt is ambiguous at best.

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