

Kinetics of Acid and Base Hydrolysis of Chloro and Bromo (Benzylamine) Bis-(Ethylene Diamine)Cobalt(III) Complexes

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The acid and base hydrolysis reactions of chloro and bromo(benzylamine)bis(ethylenediamine) Cobalt-complexes have been studied. The rate constants for the acid hydrolysis reaction of the chloro and bromo complexes at 50°C are found to be 4.5×10^{-6} and 1.8×10^{-5} (sec.^{-1}). These are found to be independent of hydrogen ion concentration between 5.0×10^{-4} to 5.0×10^{-2} M perchloric acid. The second order rate constants for base hydrolysis of the chloro and bromo complexes at 0° are 1.00 and 4.00 $\text{mole}^{-1} \text{sec.}^{-1}$ respectively. The activation parameters, E_A and S^* for the acid hydrolysis reaction of the chloro and bromo complexes are found to be 24.8, 27.0 Kcal/mole and -8.0 and +1.8 eu. respectively.

Introduction

Solvolytic aquation and base hydrolysis reactions of halopentamine Cobalt(III) complexes are well known. Acid hydrolysis (aquation) reactions of these complexes are generally independent of hydrogen ion concentration below pH 4.0, except for the aquation of some fluoro complexes¹ which are acid catalysed presumably due to the protonation of the departing ligand. For the unusual reactivity of the hydroxide ion in the base hydrolysis reactions of such complexes two distinct mechanistic pathways, both involving some form of pre-equilibrium, have been invoked. Tobe, Chan^{2,3} and co-workers have postulated an ion-pair pre-equilibrium, the hydroxide ion being specially favoured to take up a position in the first solvation shell by a Grottaus chain transfer mechanism. Basolo and Pearson,⁴ on the other hand, have suggested a conjugate base preequilibrium involving an amine proton. When a weakly basic amine containing N-H protons is co-ordinated to Cobalt(III), the N-H protons might be expected to dissociate, even in acid media, to produce kinetically significant amounts of the conjugate base particularly at higher temperature and thus accelerate the acid hydrolysis rate of the complex. With the complexes of the type chloro(aniline)bis(ethylenediamine)Cobalt(III),⁵ the result of acid hydrolysis

have been interpreted on this basis. In this context it was considered to be of interest to investigate the hydrolysis rates of complexes containing co-ordinated benzylamine which is structurally closer to but more basic than aniline. In this paper the results of the study of acid and base hydrolysis reaction of complexes of the type chloro benzylaminebis(ethylenediamine)Cobalt(III) complexes are reported.

Experimental Section

Cis-chloro(benzylamine)bis(ethylenediamine)Cobalt(III) chloride and *cis*-bromo(benzylamine)bis(ethylenediamine)Cobalt(III) bromide were prepared by the method of Bailar and Clapp⁶ starting from the corresponding *trans*-dichloro and *trans*-dibromobis(ethylenediamine)Cobalt(III) complexes respectively.

Cis-chloro(benzylamine)bis(ethylenediamine)Cobalt(III) nitrate was prepared by dissolving the chloride complex in minimum amount of ice cold water and adding ice cold concentrated nitric acid dropwise. Red crystals of the nitrate salt which separated on stirring were filtered off, washed repeatedly with alcohol and finally with ether. This process was repeated until the compound was free from ionic chloride. The crystals were dried over potassium hydroxide. Analysis: Calculated for $[\text{Co}(\text{en})_2(\text{C}_6\text{H}_5\text{CH}_2\text{NH}_2)\text{Cl}](\text{NO}_3)_6$: Co, 13.54; Cl(Co-ord.), 7.78, Found: Co, 13.65; Cl(Co-ord.), 7.81.

Cis-bromo(benzylamine)bis(ethylenediamine)Cobalt(III) nitrate was prepared as above from the corresponding bromide.

Anal. Calcd. for $[\text{Co}(\text{en})_2(\text{C}_6\text{H}_5\text{CH}_2\text{NH}_2)\text{Br}](\text{NO}_3)_2$: Co, 12.88, Br (Co-ord), 16.30, Found: Co, 12.80, Br (Co-ord), 16.07.

For measuring the acid hydrolysis reaction rates appropriate solutions were made up in volumetric flasks, painted black to avoid photocatalysis, if any, and thermostated. Aliquots were withdrawn at known intervals and chilled in ice-cold acidified acetone-water mixtures.⁷ Halide ion released by aquation was estimated by potentiometric titration with Standard solution of silver nitrate. The kinetics of halide release was usually followed upto 50 to 55 per cent of the total co-ordinated halide.

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For measuring the base hydrolysis reaction rates the complex and sodium hydroxide solutions maintained at zero degree were rapidly mixed. After the desired time interval the reaction was quenched by adding ice-cold perchloric acid to the reaction mixture in slight excess. Halide ion released by base hydrolysis was estimated potentiometrically. A corresponding «blank» titration was performed to account for the small amount of halide ion released by acid hydrolysis.

Absorption spectra of the complexes and their aquated products were measured with a Hilger «UVISPEK» Spectrophotometer using matched quartz cells. Chemicals used were of reagent grade and all solutions were prepared in double distilled water.

Results and Discussion

The absorption spectra of the complexes consist of two bands in the visible region, one around 500 m μ ($^1A_{1g} \rightarrow ^1T_{1g}$) and the second around 350 m μ ($^1A_{1g} \rightarrow ^1T_{2g}$). Such spectra are fairly typical of halo pentamine cobalt(III) complexes. The absorption maxima of the first ligand field band ($^1A_{1g} \rightarrow ^1T_{1g}$) for the chloro, bromo and the aquocomplexes occur at 530, 540 and 490 m μ respectively, in accordance with the spectrochemical order of the ligands.⁸

The apparent first order rate constant « k_1 » for the release of halide ions due to acid hydrolysis of the complexes were obtained from the slopes of the plots of $\log(V_{\infty} - V_t)$ VS time « t », where « V_t » is the volume of silver nitrate consumed after the interval « t » and « V_{∞} » is the volume calculated for the total co-ordinated halide. Representative results are collected in Table I and II.

Table I. Dependence of observed first order rate constant for the appearance of halide ion from $[\text{Co(en)}_2(\text{Benzylamine})\text{X}](\text{NO}_3)_2$ on added NaClO₄ at 0.005 M acid condition in aqueous solution at 50°

[NaClO ₄], moles/litre	Concentration of complex 0.003 M			
	0.005	0.01	0.05	0.1
X = Cl, $k_1 \times 10^6$ (Sec. ⁻¹)	4.55	4.50	4.50	4.48
X = Br, $k_1 \times 10^5$ (Sec. ⁻¹)	1.84	1.81	1.77	1.76

Table II. Dependence of observed first order rate constant for the appearance of halide ion from $[\text{Co(en)}_2(\text{Benzylamine})\text{X}](\text{NO}_3)_2$ on added HClO₄ at fixed ionic strength (0.1) in aqueous solution at 50°.

[HClO ₄] moles $\times 10^2$ /litre	Concentration of complex ~0.003 M				
	0.05	0.1	0.5	1.0	5.0
X = Cl, $k_1 \times 10^6$	4.58	4.56	4.52	4.50	4.53
X = Br, $k_1 \times 10^5$	1.79	1.84	1.81	1.78	1.80

A perusal of these results indicate that the rate constants (k_1) are practically independent of hydrogen ion concentration and ionic strength. The pK_a of ammonia (9.24) and benzylamine (9.25) are practically

identical. In view of the rapid reaction of the Cobalt amine complexes with hydroxide ion; it has not been possible to obtain reliable values of pK_a of these complexes experimentally. Basolo⁹ *et al.* have estimated the pK_a of $[\text{Co(en)}_2(\text{NH}_3)\text{Cl}]^{2+}$ to be greater than 15. Even though it is not strictly correct to correlate the pK_a of the free amine to that co-ordinated to a metal ion, in the absence of any other relations and on analogy with the results noted above, it would be reasonable to assume the pK_a of $[\text{Co(en)}_2(\text{benzylamine})\text{Cl}]^{2+}$ and the corresponding bromo complex to be greater than 15. The N-H protons of co-ordinated benzyl amine would, therefore, be hardly expected to dissociate in acid media. As such the rate constants would be independent of hydrogen ion concentration of the medium, which is in accordance with the results in Table II.

Since the N-H protons of the co-ordinated amine remain practically undissociated in the range of pH (pH ~ 1.3 to 3.3) at which this investigation was carried out, variation of ionic strength should have little effect on the acid hydrolysis rates, which is again in agreement with the results collected in Table I. The faster rate of aquation of the bromo complex is in accord with observed order of reactivity $\text{F}^- < \text{Cl}^- < \text{Br}^-$.

The base hydrolysis reactions were carried out at 0°. The second order rate constants from typical runs are collected in Table III. The bromo benzylamine complex is found to be more reactive than the chloro benzylamine complex. This correspondence in the reactivity of the chloro and bromo complexes both in acid and base hydrolysis reactions (*Vide* Table V) is suggestive of a common mechanism being operative in both processes.

Table III. Second order rate constants for base hydrolysis at 0°

[Complex] millimoles/litre	Initial ionic strength ~0.1		k_2 (mole ⁻¹ sec ⁻¹)
	[NaOH] millimoles/litre		
	$[\text{Co(en)}_2(\text{Benzylamine})\text{Cl}]^{2+}$		
1.84	1.79		0.99
1.81	3.47		1.01
1.81	5.39		1.08
	$[\text{Co(en)}_2(\text{Benzylamine})\text{Br}]^{2+}$		
2.26	1.39		4.26
2.26	1.73		3.87
2.24	1.98		4.18

In view of the increasing emphasis on the energetics of the kinetic processes, the activation energy (E_A) and the activation entropy (ΔS^*) of the acid hydrolysis reaction of the chloro and bromo benzylamine complexes have been determined (Table IV). The activation energies were calculated from the temperature dependence of the reaction rates using the Arrhenius equation. The entropy of activation was

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calculated from the equation¹⁰

$$k_1 = X \frac{kT}{h} e^{AS^*/R} \cdot e^{-E_A/RT}$$

where « X » is the transmission coefficient (taken to be unity), « k », the Boltzmann constant and « h » the Planck constant.

Table IV. Dependence of observed first order rate constant for the appearance of halide ion on temperature at 0.005 M HClO₄ and 0.1 ionic strength

Temp. (°C)	k ₁ (Sec ⁻¹) × 10 ⁵	E _A (Kcal/mole)	ΔS* (e.u.)
[Co(en) ₂ (Benzylamine)Cl] ²⁺			
50.0	4.52		
55.0	8.75	24.8	-8.0
60.0	15.5		
[Co(en) ₂ (Benzylamine)Br] ²⁺			
50.0	1.79		
54.8	3.32	27.0	+1.8
60.0	6.77		

The relative reaction rates and activation parameters for few halopentamine Cobalt(III) systems, reported earlier, are collected in Table V along with the benzylamine systems for the sake of comparison.

Higher rates of aquation for bromo complexes compared to chloro might be due to 1-2 Kcal difference in activation energy. It is interesting to note that bromo complexes have a relatively higher entropy of activation. Recently Tobe¹¹ in an attempt to visualise the nature of the intermediate in unimolecular octahedral aquation reactions, considered a large number of heat of activation (ΔH*) and entropy of activation data. He concluded that for the same departing ligand (chloride) the higher entropies of activation are diagnostic of an incipient trigonal bipyramidal intermediate and the lower values for that of an incipient tetragonal pyramid. In view of the consistently similar mechanistic behaviour of acid hydrolysis reactions of chloro and bromo complexes of Co^{III}, the negative and low positive values of the entropy of activation of the chloro and bromo benzylamine complexes respectively are indicative of a S_N1 pathway proceeding through an incipient tetragonal pyramid intermediate.

Table V. Relative reaction rates and activation parameters for some halopentamine Cobalt(III) complexes

Complex	k ₁ (Br)/k ₁ (Cl)	Temp. (°C)	Aquation		ΔS* (Br) e.u.	ΔS* (Cl) e.u.	Base Hydrolysis k ₂ (Br)/k ₂ (Cl)
			E _A (Br) Kcals	E _A (Cl) Kcals			
Co(NH ₃) ₅ X ²⁺	3.0	25	23.9	22.9	-4	-9	6.7 (25°C) ^{a b}
Cis-Co(en) ₂ (NH ₃)X ²⁺	3.4	62.6	—	22.3	—	-11	6.6 (0°C) ^{c d}
Cis-Co(en) ₂ C ₆ H ₅ CH ₂ NH ₂ X ²⁺	4.0	50	27.0	24.8	+1.8	-8.0	4.0 (0°C)

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