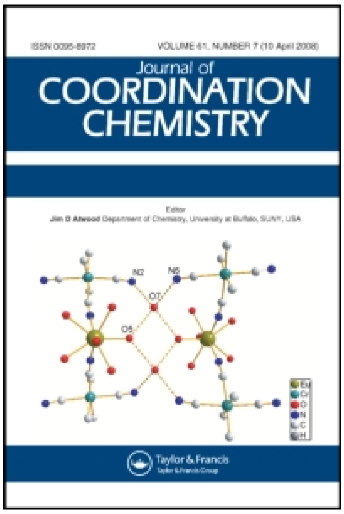

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A KINETIC STUDY OF ACID DISSOCIATION AND SOLVOLYSIS II. CHLORO, BROMO AND IODOPENTAAMMINECOBALT (III) PERCHLORATE IN LIQUID AMMONIA

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KEY WORDS: ammines; cobalt[III] ammines; ammonia, liquid; kinetics of cobalt complexes; conjugate base mechanism.

For the complexes $Co[NH_3]_5Cl[ClO_4]_2$, $Co[NH_3]_5Br[ClO_4]_4$ and $Co[NH_3]_5I[ClO_4]_2$ reaction rates to the corresponding hexaammines in liquid ammonia have been determined spectrophotometrically at a fixed electrolyte concentration of 0.2 m and at varying temperature. For the first time for the S_N1CB reaction mechanism of cobalt complexes the values of the rate determining step and of the conjugate base constant could be separated; this could be realized for the complexes $Co[NH_3]_5Cl[ClO_4]_2$ and $Co[NH_3]_5Br[ClO_4]_2$. Activation parameters of the reaction are discussed and compared to the rates of hydrolysis.

INTRODUCTION

The solvolysis products of cobalt[III] ammines in liquid ammonia have been extensively investigated by Schmitz-DuMont and co-workers.[1–4] No kinetic data about these systems have been published. A little more is known about the analogous reactions of chromium[III] complexes in liquid ammonia. From nitrogen exchange rates between $Cr[NH_3]_6[ClO_4]_3$ and ammonia Hunt and coworkers[5,6] suggested the reaction mechanism to be S_N1CB.[7] Recently[8] this mechanism has been used and extended for the analogous reaction:

$$Co(NH_3)_5Cl \cdot (ClO_4)_2 + NH_3 + KClO_4 \longrightarrow Co(NH_3)_6 \cdot (ClO_4)_3 + KCl \qquad (1)$$

Reaction rates and equilibrium constants have been reported. In this paper reaction parameters are reported for the reaction of $Co[NH_3]_5Cl[ClO_4]_2$, $Co[NH_3]_5Br[ClO_4]_2$ and $Co[NH_3]_5I[ClO_4]_2$ in liquid ammonia leading to the corresponding hexaammines.

EXPERIMENTAL PART

Materials

Chloropentaamminecobalt[III] perchlorate was prepared from the nitrate.[9] Bromopentaamminecobalt[III] perchlorate was prepared in a similar way from the bromide.[10] Iodopentaamminecobalt[III] perchlorate was prepared according to Linhard and Weigel.[9] All cobalt complexes prepared as described above were found to contain acid reacting trace impurities that interfered with kinetic measurements. The complexes could be obtained sufficiently acid-free by recrystallizing from slightly alkaline dilute borax or tris[hydroxymethyl]aminomethane solutions. Attempts to purify iodopentaamminecobalt[III] perchlorate were unsuccessful, because the complex itself decomposes rapidly in slightly alkaline solutions.

Potassium perchlorate was prepared from sodium perchlorate and potassium nitrate. To remove water enclosed in the crystals potassium perchlorate was heated during 15 minutes at 350 °C.[11] Ammonium perchlorate was reagent grade. All compounds were thoroughly dried and stored over phosphorus pentoxide. Ammonia was purified by distilling from potassium as described by Lagowski.[12]

Reaction Cells

The cells were made of stainless steel, with pyrex windows (optical path length 15 mm). As the observed reaction rates varied over four decades, it was necessary to design two types of cells:

1. A cell for moderate or slow ($t_{1/2} > 5$ min.) reactions. A double-walled cell was constructed in order to flush cold or warm nitrogen gas between the walls to cool down or warm up the cell and its contents rapidly to a desired temperature.
2. A cell suited for fast reactions ($t_{1/2} > 10$ sec.), containing an ampoule loaded with the cobalt complex. As soon as the cell and its contents (solvent and electrolyte) had reached a desired temperature, the ampoule was broken. As the cobalt complexes dissolve rapidly (in about 0.5 seconds) it was possible to follow the reaction almost instantaneously.

The cells could be placed in the cuvette room of the spectrophotometer, which was thermostatted with a Cryoson thermostat. The temperature of the solution was measured in the cell with a copper-constant thermocouple and found to be constant within 0.1°C.

Apparatus

All reactions were followed spectrophotometrically by using a Zeiss PM QII spectrophotometer, provided with a Kipp BD 9 recorder to record the change of transmission with time. From this with the help of a suitable calibration procedure the concentration of the pentaammine as a function of time was calculated.

Kinetic Runs

All concentrations will be given in molal (mol/kg solvent). The cobalt(III) ammines can be considered as 1–1 electrolytes.[13] All reactions were performed at constant ionic medium (the extensive ion-association in liquid ammonia excludes to relate this concept to the ionic strength); this was realized by keeping the total concentration of electrolytes constant (0.2 m) by adding potassium perchlorate in the experiments with chloro, bromo and iodopentaamminecobalt(III) perchlorate.

Two series of experiments were performed:

A. Experiments with added acid in the form of ammonium salts. The concentration of acid was varied at a fixed concentration of cobalt. These experiments were performed at different temperatures. Acid concentrations (of ammonium perchlorate) were varied from 0.0001 to 0.02 m in the experiments with chloropentaamminecobalt(III) perchlorate; from 0.001 to 0.15 m in the experiments with bromopentaamminecobalt(III) perchlorate and from 0.05 to 0.20 m in the experiments with iodopentaamminecobalt(III) perchlorate.

B. A series of experiments without the addition of acid. The concentration of the cobalt complex was varied to study its influence as an acid on the reaction rates. These experiments were also performed at several temperatures. Only chloro and bromopentaamminecobalt(III) perchlorate were subjected to this procedure, because iodopentaamminecobalt(III) perchlorate could not be obtained sufficiently acid free. The concentration of the cobalt complexes varied from 0.003 to 0.02 m.

Computation

All calculations were performed on a IBM 1130 computer. First order reaction rate constants and activation parameters were calculated with programs published by DeTar.[14,15] In other cases programs were written in our laboratory.

RESULTS

In all cases studied the end product was hexaammine. The observed reaction rate in all experiments was independent of the wavelength. Following the suggestion of Hunt,[5,6] the mechanism of reaction (1) in a large excess of potassium perchlorate can be formulated as follows:

$$\mathrm{Co(NH_3)_5X \cdot Y_2 + NH_3 \underset{}{\overset{K_5^{CB}}{\rightleftharpoons}} Co(NH_3)_4NH_2X \cdot Y + NH_4 \cdot Y} \quad (2)$$

$$\mathrm{Co(NH_3)_4NH_2X \cdot Y + K \cdot Y \xrightarrow{k_1} Co(NH_3)_4NH_2 \cdot Y_2 + K \cdot X} \quad (3)$$

$$\mathrm{Co(NH_3)_4NH_2 \cdot Y_2 + NH_4 \cdot Y \xrightarrow{fast} Co(NH_3)_6 \cdot Y_3} \quad (4)$$

$$\mathrm{Co(NH_3)_6 \cdot Y_3 + NH_3 \overset{K_6^{CB}}{\rightleftharpoons} Co(NH_3)_5NH_2 \cdot Y_2 + NH_4 \cdot Y} \quad (5)$$

where X = Cl, Br or I, Y = ClO_4. Ionic charges have been omitted.

Reaction (3) is the rate determining step, a dissociative elimination of the halide from the conjugate base $Co(NH_3)_4NH_2X{\cdot}Y$. Reactions (2), (4) and (5) are fast compared to reaction (3).

The following notation will be used: c_5 is the concentration of cobalt pentaammine and c_6 of the hexaammine. K_5^{CB} and K_6^{CB} are acid-base constants for the pentaammine and hexaammine respectively. k_1 is the first order rate constant of the rate determining step (3). CB_5 and CB_6 denote concentrations of conjugate bases and N_t the total concentration of acid. As CB_5 and CB_6 are very small, the total cobalt concentration c_t may be approximated by the sum of c_5 and c_6. Only neutral ion-pairs of the cobalt(III) ammines will be considered, as in all experiments an excess of neutral electrolyte has been present. By definition the observed rate s is equal to $(-dc_5)/dt$.

Now we have two cases:

1, If acid is added, the reaction is first order with an observed reaction rate constant

$$k_{obs} = k_1 \cdot K_5^{CB} \cdot (N_t)^{-1} \qquad (6)$$

Indeed all reactions with added acid at constant ionic medium and temperature obeyed a first order rate law from 0–5 to 95–100 percent reaction. Consequently the product $k_1 \cdot K_5^{CB}$ was calculated from the first order rate constant according to Eq. (6); the resulting values are shown in Table I. The results for iodopentaamminecobalt(III) perchlorate are less accurate compared to the other complexes, because the reaction for this complex could only be followed up to 75 percent completion as a side reaction under formation of iodine took place. Table II gives pseudo activation parameters for $k_1 \cdot K_5^{CB}$ for the various complexes.

2, If no acid is added, the situation is more complicated. The rate of disappearance of the cobalt pentaammine can be expressed by:

$$s = -\frac{dc_5}{dt} = k_1 \cdot K_5^{CB} \cdot c_5 \cdot [K_6^{CB} \cdot c_t + (K_5^{CB} - K_6^{CB}) \cdot c_5]^{-1/2} \qquad (7)$$

Only in the very special case that $K_5^{CB} = K_6^{CB}$ a first order rate is expected, with an observed rate constant

$$k_{obs} = k_1 \cdot (K_5^{CB})^{1/2} \cdot (c_t)^{-1/2} \qquad (8)$$

The observed first order rate constant will be proportional to the reciprocal of the square root of the total cobalt concentration.

In the case that K_5^{CB} does not equal K_6^{CB} Eq. (7) can also be simplified by considering the limiting case of zero time

$$k_{obs}(t = 0) = k_1 \cdot (K_5^{CB})^{1/2} \cdot (c_t)^{-1/2} \qquad (9)$$

TABLE I
Values of $k_1 \cdot K_5^{CB}$ for the reaction of cobalt(III) ammines in liquid ammonia at an ionic medium of 0.2 m

Complex	t(°C)	$10^6 \cdot k_1 \cdot K_5^{CB}$ (mol · kg^{-1} · sec^{-1})
$Co(NH_3)_5Cl(ClO_4)_2$	2.1	32
	−8.6	7.7
	−27.3	0.25
	−30.2	0.15
	−37.3	0.047
	−46.6	0.012
$Co(NH_3)_5Br(ClO_4)_2$	−13.4	270
	−16.2	180
	−19.0	140
	−21.8	87
	−52.6	0.65
	−55.8	0.32
	−58.9	0.16
	−62.3	0.077
$Co(NH_3)_5I(ClO_4)_2$	−30.2	15000
	−40.5	3300
	−51.5	670

This equation has the same form as Eq. (8). Values of $k_{obs}(t = 0)$ can be obtained by extrapolating k from the curve of c_5 versus time.

Reactions without the addition of acid have been performed with chloro and bromopentaammine complexes. From these only the chloro complex at constant cobalt concentration, temperature and ionic medium obeyed a first order rate law. Values of k_1 have been calculated with the Eqs. (6) and (8) and are shown in Table III. These values differ somewhat from earlier published values because the product $k_1 \cdot (K_5^{CB})^{1/2}$ has been determined more accurately now. Thermodynamic parameters are only given for k_1, as the error in K_5^{CB} is very large (about 25%) (Table IV). The kinetic results (c_5 vs time) from the bromopentaammine complex were subjected to Eq. (9) and indeed here showed the expected rate dependence on the total cobalt concentration. The

TABLE II
Pseudo activation parameters for $k_1 \cdot K_5^{CB}$

Complex	$\Delta H^{\ddagger}$ (kcal · mol^{-1})	$\Delta S^{\ddagger}$ (e.u.)
$Co(NH_3)_5Cl(ClO_4)_2$	20.9 ± 1	−3 ± 2
$Co(NH_3)_5Br(ClO_4)_2$	17.3 ± 1	−7 ± 2
$Co(NH_3)_5I(ClO_4)_2$	15.6 ± 2	−6 ± 4

TABLE III
Parameters for chloro and bromopentaamminecobalt(III) perchlorate as a function of temperature

Chloropentaamminecobalt(III) perchlorate

t (°C)	$10^8 \cdot k_1 \cdot K_5^{CB}$ (mol · kg^{-1} · sec^{-1})	$10^5 \cdot k_1 \cdot (K_5^{CB})^{1/2}$ (mol$^{1/2}$ · kg$^{1/2}$ · sec^{-1})	k_1 (sec^{-1})	$10^7 \cdot K_5^{CB}$[a] (mol · kg^{-1})
−30.2	15	55	2.13	0.7
−37.3	4.7	16	0.58	0.8
−46.6	1.2	2.8	0.07	1.8

[a] In this case $K_5^{CB} = K_6^{CB}$ (see text)

Bromopentaamminecobalt(III) perchlorate

t (°C)	$10^6 \cdot k_1 \cdot K_5^{CB}$ (mol · kg^{-1} · sec^{-1})	$10^8 \cdot \frac{(k_1 \cdot K_5^{CB})^2}{K_6^{CB}}$ (mol · kg^{-1} · sec^{-2})	$\frac{K_5^{CB}}{K_6^{CB}}$	k_1 (sec^{-1})	$10^7 \cdot K_5^{CB}$ (mol · kg^{-1})	$10^7 \cdot K_6^{CB}$ (mol · kg^{-1})
−46.6	1.8	528	0.43	7.3	2.5	6
−56.6	0.31	22.2	0.49	1.3	2.5	5
−66.5	0.04	0.22	0.49	0.13	3.5	7
−71.5	0.014	0.03	0.37	0.06	2	6

ensuing parameter values are in Table V. The fact that the Eqs. (8) and (9) were followed by the chloro and bromopentaamminecobalt(III) perchlorate respectively was taken as a proof that the compounds were acid free. In addition the slightest amounts of acid present were found to give a deviation from the Eqs. (8) and (9). Next a complete analysis of the kinetic results for the bromopentaammine complex was attempted. For the condition that $K_5^{CB} \neq K_6^{CB}$ Eq. (7) can be solved analytically,[16] but its solution is so complicated that attempts to fit experimental results failed. Therefore another procedure was followed:

$$s = -\frac{dc_5}{dt}$$

was calculated numerically from the observed curve c_5 vs time. Then

$$s^2 = \frac{p \cdot (c_5)^2}{1 + q \cdot c_5}$$

with

$$p = \frac{(k_1 \cdot K_5^{CB})^2}{K_6^{CB} \cdot c_t} \quad \text{and} \quad q = \frac{(K_5^{CB} - K_6^{CB})}{K_6^{CB} \cdot c_t} \qquad (10)$$

Equation (10) can be rearranged to

$$(c_5)^{-1} = p \cdot c_5 \cdot (s)^{-2} - q$$

so p and q can be determined by plotting $(c_5)^{-1}$ vs $c_5 \cdot (s)^{-2}$ for experiments at constant cobalt concentration. If now c_t is varied, p and q are obtained as functions of c_t. Subsequent plots of p and q vs $(c_t)^{-1}$ give the parameter combinations

$$\frac{(k_1 \cdot K_5^{CB})^2}{K_6^{CB}} \quad \text{and} \quad \frac{(K_5^{CB} - K_6^{CB})}{K_6^{CB}} \qquad (11)$$

Combining the Eq. (11) with the product $k_1 \cdot K_5^{CB}$ obtained by applying equation (6) the individual parameters k_1, K_5^{CB} and K_6^{CB} can be calculated. The complete c_5 versus t curves for the bromopentaammine complex were fitted to equation (10). In this way using the procedure described above a new set of values for the parameters k_1 and K_5^{CB} in addition to the parameter K_6^{CB} was obtained (see Table III). The errors in k_1, and K_5^{CB} as well as in K_6^{CB} are now 10 and 25 percent respectively. From the observed temperature dependence of k_1 activation parameters were calculated using a least squares procedure (Table IV).

DISCUSSION

The results obtained in this study of the kinetics of base solvolysis in liquid ammonia add essentially new material to the conjugate base mechanism as it is presently understood. In the first place the greater acid strength of the pentaammines in liquid ammonia compared to water has enabled us to separate the two rate influencing factors: the acid-conjugate base dissociation constant and the first order rate constant for the elimination of the halide ion from the

TABLE IV
Activation parameters for k_1 of chloro and bromopentaamminecobalt(III) perchlorate in liquid ammonia and for acid hydrolysis in water

	Ammonia		Water	
Complex	ΔH^{+} (kcal · mol^{-1})	$\Delta S^{\ddagger}$ (e.u.)	$\Delta H^{\ddagger}$ (kcal · mol^{-1})	$\Delta S^{\ddagger}$ (e.u.)
$Co(NH_3)_5Cl(ClO_4)_2$	22.8 ± 2	38 ± 4	23	−9
$Co(NH_3)_5Br(ClO_4)_2$	17.5 ± 1	23 ± 2	24	−4

conjugate base. Secondly the results in liquid ammonia provide a comparison between the mass of data accumulated on the reaction in water to the results from this study on the analogous reactions in the non-aqueous solvent with high coordinating power that ammonia is. The data on the combination $k_1 \cdot K_5^{CB}$ are the most reliable results and also those for which analogous data in water are available. Activation parameters have been tabulated[17] for the reaction in aqueous solution (Table VI).

$$Co(NH_3)_5X^{2+} + OH^- \longrightarrow Co(NH_3)_5OH^{2+} + X^- \qquad (12)$$

In our work it was inevitable to formulate the formation of the conjugate base as reaction (1). To make a comparison possible we have reformulated the acid-base reactions in water and liquid ammonia as:

$$Co(NH_3)_5X^{2+}(sol.) \longrightarrow Co(NH_3)_5NH_2X^{+}(sol.) + H^{+}(gas) \qquad (13)$$

We may now calculate the difference in activation parameters for the base hydrolysis in water and ammonia as defined by reaction (13). This was done in an approximate way (neglecting differences in ionic strength and association) by using the values 13.5 kcal/mol and −27 e.u. for the acid dissociation enthalpy and entropy of water[18] and −23 kcal/mol and −23 e.u. for the difference between ammoniation and hydratation enthalpy and entropy respectively for the proton.[19] We define $DH^{\ddagger} = \Delta H^{\ddagger}(water) - \Delta H^{\ddagger}(ammonia)$ and $DS^{\ddagger} = \Delta S^{\ddagger}(water) - \Delta S^{\ddagger}(ammonia)$.

TABLE V
k_1 and K_5^{CB} for bromopentaamminecobalt(III) perchlorate calculated by extrapolating to 0% reaction

t (°C)	k_1 (sec^{-1})	$10^6 \cdot K_5^{CB}$ (mol · kg^{-1})
−46.6	4.4 (7.3)[a]	0.4 (0.25)
−56.6	2.9 (1.3)	0.1 (0.25)
−66.5	0.08 (0.13)	0.5 (0.35)

[a] In parentheses the values of k_1 and K_5^{CB} calculated from the complete set of data.

TABLE VI
Activation parameters for base hydrolysis of $Co(NH_3)_5X^{2+}$ complexes and $DH^{\ddagger}$ and $DS^{\ddagger}$ values[a]

X	$\Delta H^{\ddagger}$ (kcal · mol^{-1})	$\Delta S^{\ddagger}$ (e.u.)	$DH^{\ddagger}$ (kcal · mol^{-1})	$DS^{\ddagger}$ (e.u.)
Cl	29	36	−1.4	−11
Br	28	40	1.2	−3
I	29	42	3.9	−2

[a] for definition see text.

The $DH^{\ddagger}$ and $DS^{\ddagger}$ values calculated in this way are presented in Table VI. The differences are not dramatic. This means that an important factor responsible for the higher solvolysis rates in ammonia compared to water is the more favourable heat of solvation of the proton in ammonia.

Also the separate values for k_1 and K_5^{CB} in liquid ammonia are now available. As a similar separation for the base hydrolysis in water is impossible,[20] a direct comparison water-ammonia cannot be made in this respect. However, it is instructive to compare the enthalpy values of k_1 in ammonia with values published for the analogous aquation reactions, that also has a dissociative interchange mechanism.[21] The values in Table IV have been taken from tabulations by Basolo and Pearson;[22] more recent investigations[23] confirm these values. The most striking result is that $\Delta H^{\ddagger}$ values for both systems are in the same range. This result seems to indicate that the high reactivity of the conjugate base is not primarily due to a weakening of the bond to the leaving group. The decisive factor seems to be the entropy. Following Tobe[24] in his discussion about aquation reactions, this may reflect a high degree of rearrangement of the first and probably also the second coordination sphere forming the activated complex. This is in agreement with the extensive steric rearrangement generally observed in base hydrolysis.[20] In the last place from the rather inaccurate values of K_5^{CB} and

K_6^{CB} it can be concluded that these acid dissociation constants are not much dependent on the temperature. The enthalpy difference for the equilibria (2) and (5) is consequently close to zero. This is also apparent from the fact that for the same complex $\Delta H^{\ddagger}$ values for the product $k_1 \cdot K_5^{CB}$ (Table II) and for k_1 (Table IV) are equal within the experimental error. Values of K_6^{CB} for hexaamminecobalt(III) perchlorate calculated from chloro and bromopentaamminecobalt(III) perchlorate do not agree within the standard deviation. We see this as a consequence of the different approximations used.

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