2384 *Inorg. Chem.* **1985**, *24*, 2384–2388

Contribution from the Department of Chemistry,
Free University, 1081 HV Amsterdam, The Netherlands

Rate-Limiting Deprotonation in the Base-Catalyzed Ammoniation of Asymmetric *trans*-Diacidobis(ethylenediamine)cobalt(III) Perchlorates in Liquid Ammonia

SIJBE BALT,* HENDRIKUS J. GAMELKOORN, and SAMUEL OOSTERINK

Received September 24, 1984

The first step of ammoniation of asymmetric *trans*-$[Co(en)_2YX]ClO_4$ (with Y = N_3, –NCS; X (leaving group) = Cl, Br) was studied in liquid ammonia. The reactions generally follow the conjugate-base mechanism. In the case of the azido chloro, the azido bromo, the isothiocyanato chloro, and presumably the isothiocyanato bromo complexes, there is competition between the elimination of the leaving group and the reprotonation of the conjugate base in the accessible acidity range of the medium. The *trans*-$[Co(en)_2YX]^+$ series provides the first examples of asymmetric trans systems with rate-limiting deprotonation. Activation parameters for the overall two-stage process ($K^{CB}k_2$) are as follows (expressed as YX (ΔH^* in kJ mol^{-1}; ΔS^* in J K^{-1} mol^{-1})): (N_3)Cl (69; –34), (N_3)Br (62; –45), (NCS)Cl (66; –52). The values of the activation parameters do not have diagnostic value for the mechanism. The proton-transfer processes of the complexes were investigated by ^{1}H NMR spectroscopy. Separate resonances and ^{1}H–^{2}H transfer rates for hydrogen at each side of the CoN_4 plane were observed. The results indicate that only deprotonation at one of the sides leads to a reactive conjugate base. In general the steric course of the ammoniation reactions is remarkably similar to that of the corresponding base hydrolysis reactions, including a leaving-group effect. The observation of rearrangement is novel for systems with rate-limiting deprotonation.

Introduction

As part of our studies on the application of the two-step conjugate-base (CB) mechanism[1] to base-catalyzed ammoniation reactions in liquid ammonia we have reported that *trans*-$[Co(NH_3)_4Cl_2]^+$ and *trans*-$[Co(en)_2Cl_2]^+$ (en = ethylenediamine) exhibit rate-limiting deprotonation.[2] These results seem to suggest that, just as for base hydrolysis,[3,4] the complexes that demonstrate rate-limiting deprotonation in liquid ammonia are of the *trans*-$[CoL_4X_2]^+$ type, where L_4 is a four-nitrogen donor set and X is a halide or pseudohalide.

A more complete picture of the reaction mechanism may be obtained from the steric course of the reaction under investigation. We have been able to show that the first step of ammoniation of both *trans*-$[Co(NH_3)_4Cl_2]ClO_4$ and *trans*-$[Co(en)_2Cl_2]ClO_4$ in liquid ammonia, similar to the base hydrolysis, proceeds under retention of configuration,[5] contrary to the general picture for a base-catalyzed reaction, which is usually accompanied by substantial rearrangement.[6]

We present here a study of kinetics and steric course of the base-catalyzed ammoniation of three asymmetric *trans*-$[Co(en)_2YX]ClO_4$ complexes (YX = (N_3)Cl, (N_3)Br, (NCS)Cl), giving evidence of rate-limiting deprotonation. Proton-exchange rates were obtained for these complexes and were compared with the photometrically determined ammoniation rates.

Experimental Section

Materials. *trans*-$[Co(en)_2(N_3)Cl]ClO_4$,[7] *trans*-$[Co(en)_2(N_3)Br]ClO_4$,[7] *trans*-$[Co(en)_2(N_3)(Me_2SO)](ClO_4)_2$,[7] *trans*-$[Co(en)_2(NCS)Cl]ClO_4$,[8] and *trans*-$[Co(en)_2(NCS)Br]ClO_4$[8] were prepared essentially as described in the literature. To obtain the acid-free perchlorates, the complexes were dissolved in a slightly alkaline solution and collected in a saturated aqueous solution of sodium perchlorate. Isomeric purity was checked by routine UV/vis and NMR analysis. Elemental analyses of cobalt, chlorine (Cl^-, ClO_4^-), and bromine gave satisfactory results. Liquid ammonia, perdeuterated ammonia, potassium perchlorate, and ammonium perchlorate were used as described previously.[2] All solids were dried thoroughly before use.

Kinetic Measurements. The ammoniation reactions were followed in a closed system under dry nitrogen gas. A detailed description of the apparatus and the data-processing procedure has been given elsewhere.[2] All kinetic runs were performed under a constant external pressure of 10 bar and at a constant "ionic medium" of 0.20 mol kg^{-1}, realized by the addition of calculated amounts of potassium perchlorate. In this medium the cationic cobalt(III) complexes are virtually completely ion associated. For the systems under investigation, a constant ionic medium is equivalent to a constant concentration of the (mononegative) counterions. The extensive ion association excludes a calculation of the ionic strength.[9] The ammonium perchlorate concentration was varied between 0.005 and 0.20 mol kg^{-1} at a fixed complex concentration of 0.003 mol kg^{-1} for the azido complexes and 0.010 mol kg^{-1} for the isothiocyanato chloro complex. From repetitive-scan spectra it was seen that in the ammoniation of the complexes the substitution of the chloro or bromo ligand could be monitored separately from the subsequent substitution of the azido or the isothiocyanato ligands. From the scans the optimal wavelength for monitoring the kinetics was selected: 584 nm for *trans*-$[Co(en)_2(N_3)Cl]ClO_4$, 510 nm for *trans*-$[Co(en)_2(N_3)Br]ClO_4$, and 550 nm for *trans*-$[Co(en)_2(NCS)Cl]ClO_4$. It was verified that the optical instrument did not have an observable drift for the duration of the experiments.

The mean deviation of the fit to a first-order rate law was better than 0.5% in all runs. No systematic trends in the residual absorbances were observed for at least 3 half-lives. Individual rate constants could be reproduced within 2%. The constancy of the temperature was better than 0.05 °C.

NMR Measurements. Proton-exchange rates for the azido chloro, the azido bromo, and the isothiocyanato chloro complexes in N^2H_3 were obtained as described previously.[2] The disappearance of the ^{1}H signal obeyed a first-order rate law within the limits of accuracy of the ^{1}H resonance integrals (3%). The estimated accuracy of the exchange rate constants is ±10%. The steric course of the ammoniation reactions was calculated from the integrated ^{1}H NMR resonances of the reaction products. The spectra were recorded on a Bruker WM-250 spectrometer in the reaction medium by using the technique of saturating the solvent peak before acquisition. Solutions were made up in 5-mm-diameter NMR tubes by condensation at –78 °C of about 0.5 mL of NH_3 (enriched with 5% N^2H_3 as internal lock) onto 25 mg of the acid-free complex. The ammoniation reactions were performed at –40 ± 5 °C, after which the spectra of the end products were recorded at –70 °C, in order to minimize the exchange of trans NH_3 protons between the complex and the irradiated solvent. The product distribution could be reproduced within an error of 2% absolute in this way. To check the acid independence of the steric course, control series were performed with excess (0.02 and 0.7 mol kg^{-1}) ammonium perchlorate.

Results

Reaction Kinetics. In a previous paper[2] we have worked out the complete conjugate-base reaction mechanism for the base-catalyzed ammoniation reaction. For the present case the essential steps are

---

[1] Tobe, M. L. In "Advances in Inorganic and Bioinorganic Mechanisms"; Sykes, A. G., Ed.; Academic Press: New York, 1983; Vol. 2, p 1.

[2] Balt, S.; Gamelkoorn, H. J.; Kuipers, H. J. A. M.; Renkema, W. E. *Inorg. Chem.* **1983**, *22*, 3072.

[3] Ahmed, E.; Tucker, M. L.; Tobe, M. L. *Inorg. Chem.* **1975**, *14*, 1.

[4] Reference 1, p 10.

[5] Balt, S.; Breman, J.; de Kieviet, W. *J. Inorg. Nucl. Chem.* **1979**, *41*, 331.

[6] Basolo, F.; Pearson, R. G. "Mechanisms of Inorganic Reactions", 2nd ed.; Wiley: New York, 1967.

[7] Jackson, W. G.; Begbie, C. M. *Inorg. Chim. Acta* **1982**, *60*, 115.

[8] Werner, A. *Justus Liebigs Ann. Chem.* **1912**, *386*, 136, 148.

[9] Balt, S.; Jelsma, A. *Inorg. Chem.* **1981**, *20*, 733.

0020-1669/85/1324-2384$01.50/0

$$[\mathrm{Co(en)_2YX}]\mathrm{ClO_4} + \mathrm{NH_3} \underset{k^0_{-1}}{\overset{k^0_1}{\rightleftharpoons}} [\mathrm{Co(en)(en\text{-}H)YX}] + \mathrm{NH_4ClO_4} \quad (1)$$

$$[\mathrm{Co(en)_2YX}]\mathrm{ClO_4} + \mathrm{KNH_2} \underset{k^1_{-1}}{\overset{k^1_1}{\rightleftharpoons}} [\mathrm{Co(en)(en\text{-}H)YX}] + \mathrm{NH_3} + \mathrm{KClO_4} \quad (2)$$

$$[\mathrm{Co(en)(en\text{-}H)YX}] \xrightarrow{k_2} [\mathrm{Co(en)(en\text{-}H)Y}]\cdot\mathrm{X} \quad (3)$$

where en-H represents deprotonated ethylenediamine. Reactions 1–3 must be formulated for each individual deprotonation route. For asymmetric bis(ethylenediamine) complexes the hydrogens can be divided into two groups of four, directed either to the X (chloro or bromo) ligand or to the Y (azido or isothiocyanato) ligand. To reduce the complexity of the rate equations, it will first be assumed that only one of the two sets of four equivalent proton sites is active in the ammoniation reaction. Then, under conditions of excess acid (ammonium perchlorate), a first-order rate law will be expected, with the pseudo-first-order rate constant k_{obsd} given by eq 4, where $n = 4$. (k^1_1 is redefined[2] to suit the conditions of excess $\mathrm{NH_4ClO_4}$.)

$$k_{\mathrm{obsd}} = \frac{(nk^0_1 + nk^1_1[\mathrm{NH_4ClO_4}]^{-1})k_2}{k^0_{-1}[\mathrm{NH_4ClO_4}] + k^1_{-1} + k_2} \quad (4)$$

In Figures 1–3 the observed rate constants for the ammoniation reactions in liquid ammonia are plotted as a function of the reciprocal concentration of added ammonium perchlorate (part B). The low $[\mathrm{NH_4ClO_4}]^{-1}$ range is plotted on an enlarged scale as part A.

As the right-hand side of eq 4 is fixed by three independent parameters, the complete set of k_{obsd} vs. $[\mathrm{NH_4ClO_4}]^{-1}$ data for the three cases was subjected to a three-parameter fit on the basis of eq 4 by use of a Marquardt fitting routine.[10] For the azido chloro and the isothiocyanato chloro complexes at all temperatures, the mean deviation of the fit was less than 3%. For the azido bromo complex a similar accuracy could only be obtained by adding a constant term, k_0, to eq 4. This is certainly no evidence for a spontaneous ammoniation, as the ammoniation rate at very large ammonium perchlorate concentrations (2 mol kg^{-1}, outside the value of 0.20 chosen for the ionic medium) turned out to be less than 10% of the extrapolated k_0 value, while ionic strength effects are small (see below). The cause of this k_0 term remains uncertain. The fitting parameters yield the kinetic parameters k^0_1 and k^1_1 and the ratio $k_2{:}k^0_{-1}$, when the ratio $k_2{:}k^1_{-1}$ is expressed in these parameters by using the additional relation $k^0_1{:}k^0_{-1} = k^1_1{:}k^1_{-1}$. The values obtained are presented in Table I, together with the calculated value of the derived combination $K^{\mathrm{CB}}k_2$. Here K^{CB} is the conventional apparent acid dissociation constant,[9] defined by eq 5. Activation parameters were obtained from a

$$K^{\mathrm{CB}} = nk^0_1{:}k^0_{-1} \quad (5)$$

weighted least-squares fitting.[11] No curvature was found; the results also presented in Table I. Exactly as outlined for the case of the *trans*-$[\mathrm{Co(NH_3)_4Cl_2}]^+$ ion,[2] the denominator parameter $k_2{:}k^0_{-1}$ is the least accurate (estimated ±10%); for the other parameters the accuracy is estimated to be better than 5%. For a comparison Figures 1–3 exhibit drawn lines calculated from the parameter values obtained.

It is important to note that, contrary to an earlier report from our laboratory[12] using a more limited acid concentration range, the contribution from the acid-dependent deprotonation (eq 2, parameter k^1_1) is certainly not negligible: at the lowest ammonium perchlorate concentrations used the contributions from eq 1 and 2 are about equal.

Exchange Rates from ^{1}H NMR. ^{1}H–^{2}H exchange rates of the amine (en) hydrogens were measured by dissolving the complexes in perdeuterated ammonia under such conditions (high acidities) that the reprotonation reaction—governed by the term $k^0_{-1}\cdot[\mathrm{NH_4ClO_4}]$ in eq 4—is fast compared to the subsequent elimination reaction (k_2). This condition was verified by following the reactions in $\mathrm{NH_3}$ in the same ionic medium. The complexes show different chemical shifts for each set of four equivalent H–N hydrogens (located on coordinated $\mathrm{H_2N{-}CH_2{-}CH_2{-}NH_2}$; the corresponding bands do not coalesce on raising the temperature). The different ethylenediamine conformations are averaged out on the NMR scale. Unequivocal assignments are possible from the fact that *trans*-$[\mathrm{Co(en)_2(N_3)X}]^{n+}$ complexes in liquid ammonia invariably have one of the ^{1}H–N(en) resonances at a position only slightly (±0.1 ppm) affected by the nature of X. This resonance consequently was assigned to the H at the side of the azido ligand. A similar situation exists for the isothiocyanato complexes.[13] The fact that inequivalent hydrogen sites exchange at different rates, but strictly obey a first-order rate law, excludes rapid proton exchange between the sites in the conjugate base. This is worked out more fully in a separate communication about ^{1}H–^{2}H exchange in $\mathrm{N^2H_3}$ for a series of *trans*-bis(ethylenediamine)cobalt(III) complexes.[14] The results in terms of the first-order rate constant k_{ex} are summarized in Table II.

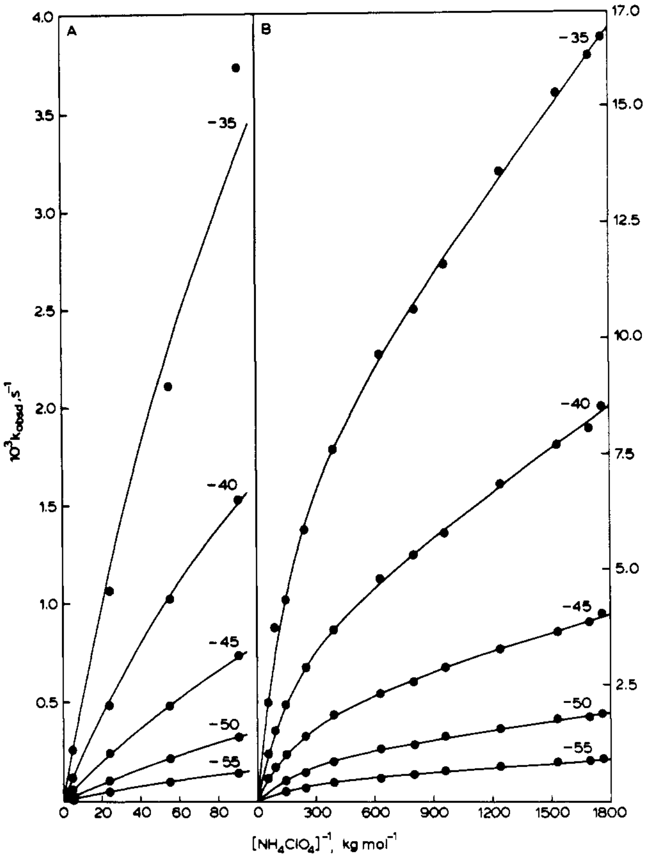

Figure 1. Variation of the observed photometric rate constant of ammoniation with the reciprocal of the ammonium perchlorate concentration for *trans*-$[\mathrm{Co(en)_2(N_3)Cl}]\mathrm{ClO_4}$.

Steric Course. The steric course of the ammoniation was determined from the ^{1}H NMR spectra of the products after reaction at −40 °C. No variation with the ammonium perchlorate concentration was observed within the experimental error. The products were identified as a mixture of *cis*- and *trans*-$[\mathrm{Co(en)_2(NH_3)Y}]^{2+}$ complexes. The obtained results are given in Table III.

Discussion

Analysis of the medium dependence of the rate of ammoniation, according to eq 4, leads to the conclusion that reprotonation of

---

(10) Fletcher, R. Report 6799; Atomic Energy Research Establishment: Harwell, Berkshire, England, 1971.

(11) Detar, C. F. "Computer Programs for Chemistry"; Benjamin: New York, 1969; Vol. III, program ACTENG.

(12) Kuipers, H. J. A. M. Ph.D. Thesis, Free University, 1983.

(13) Balt, S.; Gamelkoorn, H. J.; Lammers, K. *Transition Met. Chem.*, in press.

(14) Balt, S.; Gamelkoorn, H. J. *Inorg. Chim. Acta* **1985**, *98*, L57.

Table I. Kinetic Parameters for the Ammoniation of *trans*-[Co(en)$_2$YX]ClO$_4$

	temp, °C	$10^3 nk^0_1$, s^{-1}	$10^6 nk^1_1$, mol kg^{-1} s^{-1}	$10^3 k_2{:}k^0_{-1}$, mol kg^{-1}	$10^5 K^{CB} k_2$,[a] mol kg^{-1} s^{-1}	$k_2{:}k^1_{-1}$[a]
			trans-[Co(en)$_2$(N$_3$)Cl]ClO$_4$			
	−35.00	9.3	6.0	5.9	5.5	9
	−40.00	4.8	3.2	4.9	2.4	8
	−45.00	2.7	1.3	4.0	1.1	8
	−50.00	1.50	0.57	3.0	0.46	8
	−55.00	0.74	0.29	2.8	0.20	7
$\Delta H^{\ddagger}$ [b]		52 ± 3	65 ± 3		69 ± 3	
$\Delta S^{\ddagger}$ [c]		−64 ± 6	−68 ± 7		−34 ± 6	
			trans-[Co(en)$_2$(N$_3$)Br]ClO$_4$			
	−45.00	6.7	0.95	20	13	140
	−50.00	3.1	0.83	26	7.9	100
	−55.00	1.5	0.27	20	3.0	110
	−60.00	0.63	0.20	27	1.7	85
	−65.00	0.26	0.13	20	0.5	40
$\Delta H^{\ddagger}$ [b]		62 ± 3	41 ± 10		62 ± 6	
$\Delta S^{\ddagger}$ [c]		−12 ± 7	−176 ± 30		−45 ± 15	
			trans-[Co(en)$_2$(NCS)Cl]ClO$_4$			
	−35.00	30.9	12.8	1.1	3.4	2.7
	−40.00	13.2	7.5	1.2	1.6	2.1
	−45.00	5.4	3.7	1.4	0.73	2.0
	−50.00	2.3	1.7	1.4	0.33	1.9
	−55.00	0.84	0.79	1.8	0.15	1.9
$\Delta H^{\ddagger}$ [b]		76 ± 3	59 ± 3		66 ± 3	
$\Delta S^{\ddagger}$ [c]		45 ± 6	−88 ± 6		−52 ± 7	

[a] Calculated value. [b] In units of kJ mol^{-1}. [c] In units of J K^{-1} mol^{-1}.

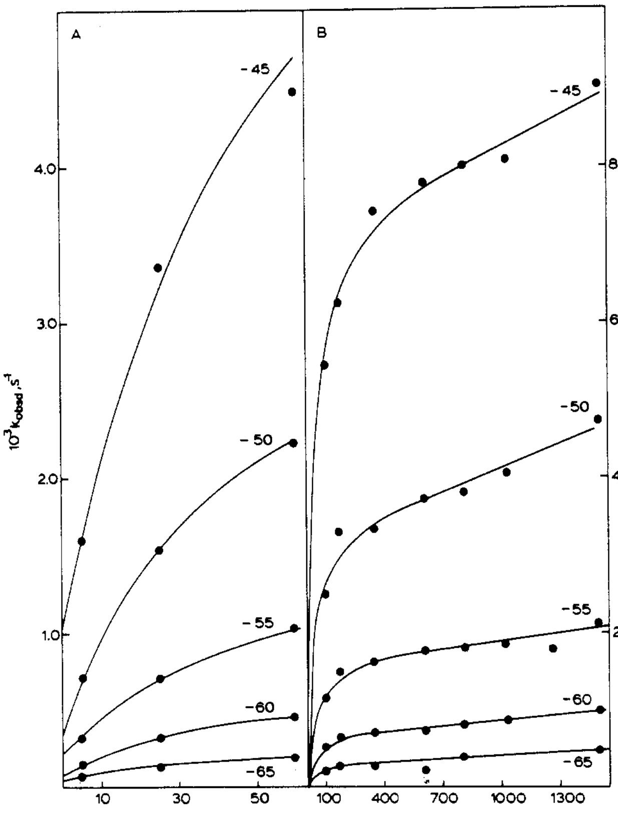

Figure 2. Variation of the observed photometric rate constant of ammoniation with the reciprocal of the ammonium perchlorate concentration for *trans*-[Co(en)$_2$(N$_3$)Br]ClO$_4$.

Table II. ^{1}H–^{2}H Exchange Rate Constants (k_{ex})[a] for *trans*-[Co(en)$_2$YX]ClO$_4$ Complexes in Liquid Ammonia and Comparison with Photometric Deprotonation Constants (k^0_1)

Y; X	temp, °C	position	δ[b]	$10^4 k_{ex}$, s^{-1}	$k_{ex}{:}k^0_1$[c] $n = 4$[d]	$k_{ex}{:}k^0_1$[c] $n = 8$[d]
N$_3$; Cl	−50.5	Cl	5.57	4.0	1.2	1.5
		N$_3$	5.35	1.1	0.3	
N$_3$; Br	−56.5	Br	5.63	3.6	1.2	1.8
		N$_3$	5.34	1.8	0.6	
NCS; Cl	−50.0	Cl	5.40	3.5	0.6	1.5
		NCS	6.13	5.1	0.9	

[a] Medium: [NH$_4$ClO$_4$] = 0.50, [ClO$_4^-$]$_{tot}$ = 0.60 mol kg^{-1}. [b] Chemical shift relative to the solvent signal. [c] k^0_1 values (extrapolated) from Table I. [d] Number of deprotonation sites leading to ammoniation.

Table III. Steric Course of Solvolysis Reactions of *trans*-[Co(en)$_2$YX]$^{2+}$ Complexes

	% steric retention		
Y; X	NH$_3$[a]	H$_2$O[b]	base hydrolysis[b,c]
N$_3$; Cl	85	91[d]	76
N$_3$; Br	78	91[d]	74
N$_3$; Me$_2$SO	70	92[d]	69.5
NCS; Cl	30	40[e]	30
NCS; Br	24	55[f]	25

[a] This work; −40 °C. [b] At 25 °C. [c] Jackson, W. G.; Begbie, C. M. *Inorg. Chem.* **1984**, *23*, 659. [d] Jackson, W. G.; Begbie, C. M. *Inorg. Chim. Acta* **1982**, *60*, 115. [e] Jordan, R. B.; Sargeson, A. M. *Inorg. Chem.* **1965**, *4*, 433. [f] Baldwin, M. E.; Tobe, M. L. *J. Chem. Soc.* **1960**, 4275.

the conjugate base and elimination of X are competitive processes for the complexes *trans*-[Co(en)$_2$YX]ClO$_4$, with YX = (N$_3$)Cl, (N$_3$)Br, and (NCS)Cl. This conclusion may be extended to *trans*-[Co(en)$_2$(NCS)Br]ClO$_4$, which proved to react too rapidly for a reliable study of medium and temperature dependences. In this respect the systems presented here behave similarly to *trans*-[Co(NH$_3$)$_4$Cl$_2$]ClO$_4$, reported earlier.[2] For a general discussion about liquid ammonia as reaction medium, the presence of general-base catalysis, the impossibility of a concerted mechanism (the reversibility of reactions 1 and 2), and the poor diagnostic value of the activation parameters,[15] we may therefore refer to the earlier report.[2]

A novel feature of the present systems is the asymmetry of the complex cations and the absence of complete stereochemical re-

---

(15) Lichtig, J.; Sosa, M. E.; Tobe, M. L. *J. Chem. Soc., Dalton Trans.* **1984**, 581.

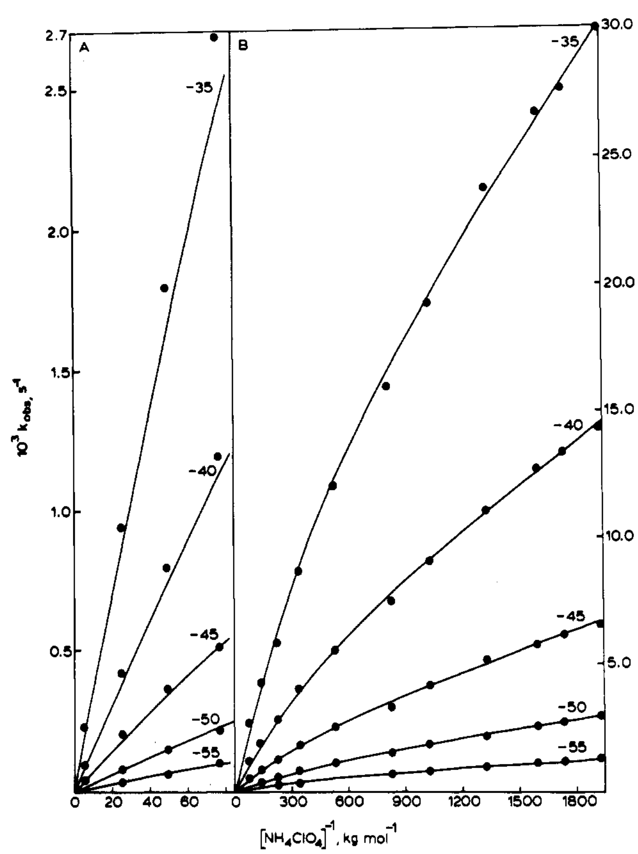

Figure 3. Variation of the observed photometric rate constant of ammoniation with the reciprocal of the ammonium perchlorate concentration for *trans*-$[Co(en)_2(NCS)Cl]ClO_4$.

tention. Until now axial symmetry and steric retention seemed to be characteristic of systems reacting by rate-limiting deprotonation.[16,17]

A further proof of the mechanism would have been the demonstration of the fact that only one proton is exchanged during the act of ammoniation. This kind of experiment is not possible for the present series of complexes, for which the reaction products were found to exchange their protons much more rapidly than the ammoniation of the original ion. A more indirect test of the proposed mechanism is the identity of ammoniation and $^1H-^2H$ exchange rates. For this comparison the necessary difference in ionic medium (0.20 mol kg^{-1} for the ammoniation and 0.60 mol kg^{-1} for the exchange) is unimportant, as proved for the $[Co(en)_2Cl_2]^+$ ion.[12] However, a solvent isotope effect $k(N^2H_3):k(N^1H_3)$ may be expected. For the dichloro complex mentioned, a value of 1.23 for this ratio has been found in our laboratory.[12] In Table II values of the ^1H NMR exchange constant (k_{ex}) are compared to the (extrapolated) photometrically determined $k^0{}_1$ values. This was done for the case where deprotonation at one ($n = 4$) or both sites ($n = 8$) of the initial cation is supposed to lead to a reactive conjugate base. The assumption of reactive deprotonation at both sites of the complex needs some comment. It means in general that the simplicity of eq 4 is lost. However, for the limiting case of rate-determining deprotonation the modified eq 4 simplifies to eq 6, where (X) and (Y) denote the

$$k_{obsd} = 4k^0{}_1(X) + 4k^0{}_1(Y) + 4[k^1{}_1(X) + k^1{}_1(Y)][NH_4ClO_4]^{-1} \quad (6)$$

side of the complex where the act of deprotonation occurs. Consequently the extrapolated value of $k^0{}_1$ can be seen as a simple sum. It is also important to note that the ratio $k_{ex}:k^0{}_1$ may be reduced by a statistical factor, $1 - p$, introduced by Anderson et al.[19] Here p is the probability of reentry of the abstracted proton. For N^2H_3 as proton abstractor (eq 1) the statistical expectation value of p is 0.25.[12]

From the entries in Table II it is obvious that all values for $k_{ex}:k^0{}_1$ calculated on the assumption that $n = 8$ (1.5, 1.8, and 1.5) are too large. On the other hand some of the entries for $n = 4$ are too small. This means that reactive deprotonation is limited to one identifiable side. For the azido complexes this is the side of the leaving group; for the isothiocyanato complex it is the reverse side. It is tempting to relate this reversion in the deprotonation side with the difference in steric course between azido and isothiocyanato complexes. This discrepancy loses its explanatory power, if the amido group in the 5-coordinate intermediate becomes planar.[1,6]

It is satisfying that for all three complexes the ratio $k_{ex}:k^0{}_1$ (1.2, 1.2, and 0.9, respectively) is close to the expected value of the isotope effect (1.23), as introduced above. Then, similarly to the case of *trans*-$[Co(NH_3)_4Cl_2]^+$,[2] we have approximately $p = 0$, meaning that between deprotonation and reprotonation the second coordination sphere rearranges sufficiently to prevent reentry of the abstracted proton.

The steric course on ammoniation deserves some comment. From Table III it is clear that there is a close parallel between the steric course of base-catalyzed ammoniation and base hydrolysis (both clearly differing from the steric course of spontaneous aquation). Also, the influence of the leaving group, recently described for base hydrolysis[20] and unexpected for a pure D type mechanism, is repeated by the ammoniation reactions. The first comment to make is that the solvent independence of the stereochemistry of base-catalyzed solvolysis of (amine)cobalt(III) complexes, to which we drew attention in earlier publications,[5,21,22] is repeated here. This may be taken to imply that the existence of one or more discrete intermediates of reduced coordination number is a reasonable assumption.[21] Our second comment is the fact that the steric course does not depend greatly on the leaving group implies dissociative activation. The slight dependence on the nature of the leaving group can then be explained from the assumption, introduced by Sargeson and co-workers,[23] that the solvent sheet of the substrate remains essentially intact during the activation and the formation of the pentacoordinate intermediate. The presence of the leaving group will then influence the position of entry of the solvent. Jackson and Begbie have postulated this mechanism for the base hydrolysis of the complexes under study.[20] For brevity we therefore refer to the report mentioned[20] for further arguments, comments, and references. It can be added that our ammoniation results seem to rule out other mechanistic interpretations of the leaving-group effect more definitely than has been possible for base hydrolysis. Here we refer to (1) preisomerization, which can be rejected by the fact that the corresponding cis complexes generally ammoniate more slowly but exchange their protons much more rapidly than the trans complexes, and (2) the postulate of more conjugate bases in the mechanistic scheme, giving stereochemically different products, which is refuted by the conclusion of reactive deprotonation at only one of the two inequivalent proton sites, drawn from the values of $k_{ex}:k^0{}_1$ as discussed above. Further, the ratio $k^0{}_1:k^1{}_1$ will be different for each separate proton site.[14,24] This would make the steric course pH dependent under the postulate

---

(16) Tobe, M. L. In "Coordination Chemistry, 20"; Banerjea, D., Ed.; Pergamon Press: Oxford, 1980; p 47 and references therein.

(17) The simplicity of the steric course is probably only apparent, as double substitution seems to be a common phenomenon in the base hydrolysis of (ethylenediamine)cobalt(III) complexes that have two easily leaving ligands. We have observed this mechanism for a number of these systems in liquid ammonia, after the demonstration of base hydrolysis by Jackson and Begbie[18] came to our knowledge.

(18) Jackson, W. G.; Begbie, C. M. *Inorg. Chem.* **1983**, *22*, 1190.

(19) Anderson, J. S.; Briscoe, H. V. A.; Spoor, N. L. *J. Chem. Soc.* **1943**, 361.

(20) Jackson, W. G.; Begbie, C. M. *Inorg. Chem.* **1984**, *23*, 659.

(21) Balt, S.; Gamelkoorn, H. J.; Renkema, W. E. *J. Chem. Soc., Dalton Trans.* **1983**, 2415.

(22) Balt, S.; Gamelkoorn, H. J. *J. Chem. Soc., Dalton Trans.* **1985**, 659.

(23) Dixon, N. E.; Jackson, W. G.; Marty, W.; Sargeson, A. M. *Inorg. Chem.* **1982**, *21*, 688.

(24) Balt, S.; Renkema, W. E.; van Zijl, P. C. M. *Inorg. Chim. Acta* **1980**, *45*, L241.

that each deprotonation site generates its own conjugate base. This was not observed. In view of the mechanism found for the ammoniation of the azido and isothiocyanato complexes, it is remarkable that there are no indications for rate-limiting deprotonation on base hydrolysis of these compounds.[25]

Acknowledgment. This work has benefited much from preliminary studies in which Dr. W. E. Renkema and Dr. H. J. A. M. Kuipers have participated.

Registry No. *trans*-$[Co(en)_2(N_3)Cl]ClO_4$, 30051-75-3; *trans*-$[Co(en)_2(N_3)Br]ClO_4$, 82704-31-2; *trans*-$[Co(en)_2(N_3)(Me_2SO)](ClO_4)_2$, 82768-63-6; *trans*-$[Co(en)_2(NCS)Cl]ClO_4$, 13820-98-9; *trans*-$[Co(en)_2(NCS)Br]ClO_4$, 88510-77-4; NH_3, 7664-41-7; Cl_2, 7782-50-5; Br_2, 7726-95-6; Me_2SO, 67-68-5.

---

(25) We observed that *trans*-$[Co(en)_2N_3Cl]^+$ exchanges its protons in ^2H_2O before base hydrolysis.

Contribution from the Department of Chemistry, Faculty of Science, Yamagata University, Koshirakawa-machi, Yamagata 990, Japan, and Nippon Jimuki Co., Ltd., Kanda-Ogawa-cho, Chiyoda-ku, Tokyo 101, Japan

Electrochemistry of Bis(dibenzoylmethanato)cobalt(II) in Dimethyl Sulfoxide

SETSUKO KUDO,[1] AKIO IWASE,* and NOBUYUKI TANAKA

Received March 29, 1984

The homogeneous chemical equilibria and the electrochemical behavior of bis(dibenzoylmethanato)cobalt(II) in dimethyl sulfoxide were studied by molar mass, conductivity, and ultraviolet spectral measurements, polarography, and cyclic voltammetry with a platinum electrode. It was found that $Co(dbm)_2$ was involved in the following equilibria in the solution: $Co(bi\text{-}dbm)_2 \rightleftharpoons Co(bi\text{-}dbm)(uni\text{-}dbm) \rightleftharpoons Co(dbm)^+ + dbm^-$; $Co(dbm)_2 + dbm^- \rightleftharpoons Co(dbm)_3^-$. In the above formulas, bi- and uni- mean that the ligand coordinate to the metal as bidentate and unidentate, respectively. Two waves at less negative potentials were explained as due to the two-electron reduction of different species, followed by the dissociation reactions; the first wave is mainly due to the reduction of Co(bi-dbm)(uni-dbm) and the second wave to that of $Co(bi\text{-}dbm)_2$.

Introduction

Much attention is being given to the metal complexes with β-diketones in both the pure and applied chemistry fields. In previous papers,[2-4] the voltammetric studies of bis(β-diketonato)nickel(II) complexes in dimethyl sulfoxide solutions provided useful information regarding the homogeneous chemical equilibria.

Matschiner et al.[5] studied the electrochemical behavior of bis(β-diketonato)cobalt(II) complexes of $Co(bzac)_2$, $Co(dbm)_2$, and $Co(acac)_2$[6] in nonaqueous solvents such as *N*,*N*-dimethylformamide and a mixed solvent of tetrahydrofuran-acetonitrile. According to the results, the electrochemical reduction mechanism of $Co(bzac)_2$ and $Co(dbm)_2$ was presented as

$$CoL_2 \overset{e^-}{\rightleftharpoons} CoL_2^- \overset{e^-}{\rightleftharpoons} CoL_2^{2-}$$

$$CoL_2^{2-} \rightarrow Co^0 + 2L^-$$

$$2CoL_2 + 2L^- \rightleftharpoons 2CoL_3^-$$

On the other hand, $Co(acac)_2$ was found to be irreversibly reduced in one step; however, the electrode reaction was not studied in detail.

This paper presents an investigation on the electrochemistry of bis(dibenzoylmethanato)cobalt(II) in dimethyl sulfoxide.

Experimental Section

Reagents. Dimethyl sulfoxide (Me_2SO) was the same as described previously.[7] Me_2SO was stored in a taped solvent bottle fitted with an automatically zeroing buret in a room with a low percentage of humidity. The Nakarai Chemicals tetrabutylammonium perchlorate (TBAP) purified for polarographic measurements was recrystallized once from ethanol, followed by drying in vacuo at room temperature for a minimum of 24 h. After cobalt(II) perchlorate hexahydrate was prepared by the reaction of cobalt(II) carbonate with perchloric acid,[8] it was brought to a constant weight in a desiccator over magnesium perchlorate.[9]

Bis(dibenzoylmethanato)cobalt(II) ($Co(dbm)_2$) was obtained as the monohydrate by the method available in the literature.[10]

Tris(dibenzoylmethanato)cobalt(III) ($Co(dbm)_3$) was synthesized by the same method as tris(acetylacetonato)cobalt(III).[11]

Tetrabutylammonium dibenzoylmethanate (n-$Bu_4N(dbm)$) was prepared according to the method of Buchta and Evans.[12] The salt was stored in the dark under dried nitrogen.

Apparatus and Procedures. Dc and differential-pulse (DP) polarograms were obtained with a Yanagimoto P-1000 voltammetric analyzer and a Watanabe WX-4404 X-Y recorder. The electrolysis cell for polarographic measurements reported previously[7] was modified in order to keep test solutions strictly away from atmospheric moisture. The capillary for the dropping-mercury electrode had an m value of 0.890 mg s^{-1} and a drop time, t_d, of 6.60 s at −1.0 V vs. SCE when measured in an air-free 0.05 mol dm^{-3} TBAP-Me_2SO solution at a mercury reservoir height of 50 cm. The mean current, $\bar{i}$, was measured in the case of dc polarography.

Cyclic voltammograms were obtained with a Hokuto Denko LS-1C linear scanner or an Iwatsu Denshi FG-330 function generator, a Nikko Keisoku DPGS-1 dual potentiogalvanostat, and a Riken Denshi F-32 X-Y plotter. Current-potential curves for scan rates higher than 500 mV s^{-1} were checked with an Iwatsu Denshi SS-5100 synchroscope. A Pt-button electrode (surface area 0.080 cm^2) was used as the working electrode for cyclic voltammetry. The electrolysis cell was similar to one described by Nawi and Riechel.[13]

Current-potential curves were measured with the three-electrode system at 25.0 ± 0.2 °C except for temperature-effect experiments. All the test solutions were deaerated for ca. 30 min with nitrogen gas in a thermostat before measurements. An aqueous saturated calomel electrode (SCE) was used as a reference electrode. As for the supporting electrolyte, 0.05 mol dm^{-3} TBAP was used unless otherwise stated.

Controlled-potential electrolysis was performed on a Yanagimoto VE-8 controlled-potential electrolyzer and a Nikko Keisoku NDCM-2 digital coulometer at a mercury-pool cathode at room temperature under a nitrogen atmosphere.

Conductivities were measured with a Yanagimoto MY-8 conductivity outfit at 25.00 ± 0.05 °C. The bright platinum electrode was used.

---

* To whom correspondence should be addressed at Yamagata University.

(1) Present address: Chemical Laboratory, Yamagata Building Service Co., Ltd., Iizuka-machi, Yamagata 990, Japan.
(2) Kudo, S.; Iwase, A.; Tanaka, N. *Bull. Chem. Soc. Jpn.* **1982**, *55*, 1416.
(3) Kudo, S.; Iwase, A.; Tanaka, N. *Nippon Kagaku Kaishi* **1983**, 1418.
(4) Kudo, S.; Iwase, A.; Tanaka, N. *Nippon Kagaku Kaishi* **1983**, 1539.
(5) Matschiner, H.; Tanneberg, H.; Rüttinger, H. H. *Z. Phys. Chem. (Leipzig.)* **1979**, *260*, 538.
(6) The abbreviations $bzac^-$, dbm^-, and $acac^-$ are for the enolate anions of Hbzac, Hdbm, and Hacac, respectively. Hbzac = benzoylacetone (1-phenyl-1,3-butanedione); Hdbm = dibenzoylmethane (1,3-diphenyl-1,3-propanedione); Hacac = acetylacetone (2,4-pentanedione).
(7) Kudo, S.; Iwase, A.; Tanaka, N. *Bull. Chem. Soc. Jpn.* **1981**, *54*, 207.
(8) Inoue, T. "Preparative Inorganic Chemistry"; Shokabo: Tokyo, 1949; p 54.
(9) Kolthoff, I. M.; Reddy, I. B. *J. Electrochem. Soc.* **1961**, *108*, 980.
(10) Moeller, T. *Inorg. Synth.* **1957**, *5*, 105.
(11) Moeller, T. *Inorg. Synth.* **1957**, *5*, 188.
(12) Buchta, R. C.; Evans, D. H. *Anal. Chem.* **1968**, *40*, 2181.
(13) Nawi, M. A.; Riechel, T. L. *Inorg. Chem.* **1981**, *20*, 1974.