ammine. This indicates a similar reaction rate for the two deprotonated reactants and indicates that π stabilization[4] is not a dominating feature in the base hydrolysis of the chloropentaamminecobalt(III) ion.

The extreme labilizing effect of NR_2 (R = H, alkyl) relative to other anionic species such as Cl^- and OH^- for the aquation of Cl^- in these cobalt(III) systems might then be accounted for by the alternative proposal[4] invoking the base strengths of the substituents which promoted the loss of Cl^-. Under these circumstances the rate order should be $NR_2 > OH^- > Cl^-$ which is the order usually observed.

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Kinetics and Equilibria of the Reaction of the Aquopentaamminecobalt(III) Ion with Aqueous Azide Ion–Hydrazoic Acid Buffer

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Anation of $Co(NH_3)_5OH_2^{3+}$ by N_3^- at pH ~4 follows the rate law $d[Co(NH_3)_5N_3^{2+}]/dt = k_{an}[Co(NH_3)_5OH_2^{3+}]$; k_{an} is essentially independent of $[HN_3]$ and pH and is proportional (within experimental error) to $[N_3^-]$, up to $[N_3^-] = 0.4$ *M*. Typically, $k_{an} = 6.1 \times 10^{-5}[N_3^-]$ sec^{-1} and $\Delta H^* = 26.9$ kcal mol^{-1} at 50° and ionic strength $I = 0.5$ *M*. However, detailed investigation over a wider $[N_3^-]$ range shows that ion-pair formation precedes anation and that the rate of entry of N_3^- equals the rate of water exchange for $Co(NH_3)_5OH_2^{3+}$. A specific interaction between N_3^- and the aquo ligand is suggested. The formation quotient for $Co(NH_3)_5N_3^{2+}$ is 830 M^{-1} at 25° and $I = 0.5$ *M;* the azido complex fits the Langford linear free energy relationship for the aquation of $Co(NH_3)_5X^{2+}$ species.

We have previously commented[1] upon the extraordinarily high entropy of activation (ΔS^*) associated with the acid-independent aquation pathway of the azidopentaamminecobalt(III) ion[2] and have suggested[1,3] that this may result from the specific involvement of a water molecule through hydrogen bonding to the N_3 ligand, leading in the transition state to the production of HN_3 and $Co(NH_3)_5OH^{2+}$ rather than the more electrostrictive "normal" products N_3^- and $Co(NH_3)_5H_2O^{3+}$. We now report on our attempts to clarify the situation by analysis of the kinetics and equilibria of the reverse reaction ("anation")

$$Co(NH_3)_5OH_2^{3+} + N_3^- \underset{k_{aq}}{\overset{k_{an}}{\rightleftharpoons}} Co(NH_3)_5N_3^{2+} + H_2O \qquad (1)$$

with particular attention to the influence of the ion-pairing preequilibrium[4]

$$Co(NH_3)_5OH_2^{3+} + N_3^- \overset{Q_{IP}}{\rightleftharpoons} [Co(NH_3)_5OH_2^{3+},N_3^-] \xrightarrow{k} Co(NH_3)_5N_3^{2+} + H_2O \qquad (2)$$

and to the properties of the azido complex with respect to Langford's[5] linear free energy relationship (LFER) between log k_{aq} and $-$log *Q* (where the stability constant $Q = k_{an}/k_{aq}$) for the complexes $Co(NH_3)_5X^{2+}$.

The latter aspect is of interest in another context; a similar LFER (of lower slope) exists[6] for the aquation of most ions of the series $Cr(H_2O)_5X^{2+}$, and this correlation includes the complex $Cr(H_2O)_5F^{2+}$, despite the anomalously high ΔS^* which is found[3,7] for the acid-independent aquation of this species. One might therefore ask whether complexes with anomalously high ΔS^* values in aquation *should* fit an LFER, in which case $Co(NH_3)_5N_3^{2+}$ will correlate with the other $Co(NH_3)_5X^{2+}$, or whether the apparent fit of $Cr(H_2O)_5F^{2+}$ in the Cr(III) LFER is fortuitous.

Experimental Section

Materials.—Distilled water was further purified by passage through Barnstead organic-removal and demineralizer cartridges, before use as solvent in the experiments described below.

Aquopentaamminecobalt(III) perchlorate was prepared by the method of Taube and Rutenberg[8] and checked for purity by microanalysis (*Anal.* Calcd for $CoN_5H_{17}O_{13}Cl_3$: N, 15.2; H, 3.5. Found: N, 15.2; H, 3.7) and by the absorption spectrum of the aqueous solution (ϵ 47.2 M^{-1} cm^{-1} at 490 nm; *cf.* 47.1 M^{-1} cm^{-1} reported elsewhere[9]).

Azidopentaamminecobalt(III) perchlorate was made by a procedure based on that described[10] for the chloride salt and was microanalyzed. *Anal.* Calcd for $CoN_8H_{15}Cl_2O_8$: N, 29.2; H, 3.9. Found: N, 28.8; H, 4.0. An aqueous solution of the complex had absorption maxima at 516 nm (ϵ 266) and 302 nm (ϵ 7810); these data compare favorably with those reported,[2] 520 nm (ϵ 262) and 302 nm (ϵ 7870).

Fisher and BDH Laboratory grade sodium azide was purified by recrystallization from water, washed with alcohol and then with ether, dried at 100°, and stored in a desiccator over phos-

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(1) T. W. Swaddle and E. L. King, *Inorg. Chem.*, **3**, 234 (1964).

(2) G. C. Lalor and E. A. Moelwyn-Hughes, *J. Chem. Soc.*, 1560 (1963).

(3) T. W. Swaddle, *J. Am. Chem. Soc.*, **89**, 4338 (1967).

(4) C. H. Langford and W. R. Muir, *ibid.*, **89**, 3141 (1967).

(5) C. H. Langford, *Inorg. Chem.*, **4**, 265 (1965).

(6) T. W. Swaddle and G. Guastalla, *ibid.*, **7**, 1915 (1968).

(7) T. W. Swaddle and E. L. King, *ibid.*, **4**, 532 (1965).

(8) H. Taube and A. C. Rutenberg, *J. Chem. Phys.*, **20**, 825 (1952).

(9) W. E. Jones and T. W. Swaddle, *Can. J. Chem.*, **45**, 2647 (1967).

(10) M. Linhard and H. Flygare, *Z. Anorg. Chem.*, **262**, 328 (1950).

phorus(V) oxide. Aqueous hydrazoic acid was prepared[11] by ion exchange of aqueous NaN_3 on Dowex 50W-X8 resin (H^+ form), was checked for purity by analyzing both for acid content (with standard NaOH solution) and for azide (by oxidation with excess standard Ce(IV), back-titrating with standard Fe(II)), and was made 2.5 *M* by dilution.

Stock $NaClO_4$ solution was made by neutralizing aqueous $HClO_4$ with AR NaOH pellets to pH ~7, then cooling, and diluting appropriately.

All spectrophotometric measurements were made using a Cary Model 15 spectrophotometer.

Kinetics of Anation at Ionic Strength 0.5 *M*.—Sodium azide (8.127 g) was dissolved in a little water in a 250-ml graduated flask; to the solution selected volumes of standard aqueous solutions of aquopentaamminecobalt(III) perchlorate (0.002 *M*) and of $HClO_4$ (1 *M*) were added, and the volume was adjusted to the mark with water. In this manner, solutions approximately 0.4, 0.3, 0.2, and 0.1 *M* in NaN_3, being 0.1, 0.2, 0.3, and 0.4 *M* in HN_3 and in $NaClO_4$, could be prepared, and the ionic strength *I* was in all cases 0.51 *M*. The apparent pH of these solutions (as determined using glass and standard calomel electrodes with a Beckman Research pH meter) was 4.90 at $[N_3^-] = 0.4\ M$, 4.37 at $[N_3^-] = 0.3\ M$, and 3.98 at $[N_3^-] = 0.2\ M$; since the pK_a of the aquo protons[12] in $Co(NH_3)_5OH_2^{3+}$ is 6.6 (at 25°, $I = 1.0$), it follows that at least 98% of the complex was present as the aquo as opposed to the hydroxo ion.

Samples (10–12 ml) of the solution were introduced into constricted test tubes using an all-glass syringe with a Teflon needle (it being necessary to avoid contamination with Fe(III), which gives intensely colored azido complexes) and sealed off so as to leave only 0.3–0.4 cm^3 of air space for expansion. Loss of significant amounts of HN_3 as vapor was thereby prevented.[13] The tubes were wrapped in aluminum foil to screen the photosensitive[10,14] azido complex from light and placed in a constant-temperature (±0.02°) bath. Samples were withdrawn at selected intervals and cooled promptly to 0°. Aliquots of the contents were pipetted into 100-ml volumetric flasks containing 2.0 *M* $(NH_4)_2HPO_4$ (5 ml) and the solution was made to the mark with water; the pH was such (7.85) that HN_3, which absorbs light appreciably at 302 nm, was essentially completely dissociated to the transparent azide ion. The reaction kinetics were followed by measuring at times *t* the optical absorbance A_t of these solutions at 302 nm, where $Co(NH_3)_5N_3^{2+}$ absorbs strongly while the other species present do not (ϵ 7 for the aquo complex, 0.6 for N_3^-, 0.05 for HPO_4^{2-}, nil for ClO_4^-). Usually, 10 such samples were used within a given run.

The reaction rates were found to be accurately (mean error <1%) first order in $[(NH_3)_5CoOH_2^{3+}]$ over more than 2 half-periods, and first-order rate coefficients were obtained from the equation

$$k_{an}t = \ln\,[(A_\infty - A_0)/(A_\infty - A_t)] \qquad (3)$$

The final readings, A_∞, were taken after 7–9 half-periods of the reaction, at which times the anation reaction would be considerably better than 99% complete. The visible-region spectrum showed the product to be entirely $Co(NH_3)_5N_3^{2+}$. It was found that, after excessively long reaction times (<10 half-periods), the absorbance (302 nm) of the solutions containing $Co(NH_3)_5N_3^{2+}$ and much HN_3 tended to fall slightly, evidently because of reduction of the cobalt(III) complex to cobalt(II) by HN_3 as has been shown[15] to occur for the hexaaquocobalt(III) ion

$$2Co^{3+}(aq) + 2HN_3 \longrightarrow Co^{2+}(aq) + 3N_2 + 2H^+ \qquad (4)$$

Ion-exchange studies designed to detect Co(II) and NH_4^+ after extended reaction periods under the conditions of the kinetic experiments were negative; however, stronger solutions (1.0 *M* NaN_3, 1.0 *M* HN_3, and 0.021 *M* $Co(NH_3)_5N_3^{2+}$) were shown to contain Co(II), but no Co(III), after 24 hr at 95°; a gas (evidently N_2) was also produced. In any event, the observed A_∞ values (302 nm) of the kinetic experiments agreed excellently with those calculated from the known molar absorbancy indices of N_3^-, $Co(NH_3)_5N_3^{2+}$, and the phosphate buffer. These kinetic data are summarized in Table I.

TABLE I

SPECIFIC RATE COEFFICIENTS FOR THE ANATION OF $Co(NH_3)_5OH_2^{3+}$ BY AZIDE ION IN AQUEOUS PERCHLORATE MEDIA AT $I = 0.51\ M$

Temp, °C	$[N_3^-]$, *M*	$[HN_3]$, *M*		$10^5 k_{an}/[N_3^-]$, $M^{-1}\ sec^{-1}$
65.00	0.101	0.399		40.9
	0.152	0.348		42.3
	0.202	0.298		40.5, 42.7
	0.203	0.297		41.6, 41.8
	0.302	0.198		42.7
	0.401	0.099		39.1
			Av	41.5 ± 1.0
60.00	0.201	0.299		22.7, 22.7
	0.301	0.199		22.4, 22.3
	0.400	0.100		22.0
			Av	22.4 ± 0.2
55.00	0.197	0.303		12.1
	0.203	0.297		12.1
	0.298	0.202		12.1
	0.302	0.198		12.2, 12.3
	0.348	0.158		12.0
	0.399	0.101		11.7
	0.401	0.099		11.7
			Av	12.0 ± 0.14
50.00	0.201	0.299		6.15
	0.301	0.199		6.13, 6.13
	0.400	0.100		6.04, 6.07
			Av	6.10 ± 0.04
40.00	0.201	0.299		1.60
	0.301	0.199		1.63
	0.400	0.100		1.59, 1.60, 1.61
			Av	1.60 ± 0.01

Kinetics of Anation at Ionic Strength 2.0 *M*.—The general procedure was similar to the runs made at $I = 0.5\ M$, except that the ratio $[HN_3]/[N_3^-]$ was made approximately unity in most cases, and all data were obtained for 45°. Excess aqueous HN_3 was added as such for runs at $[N_3^-] > 1.0\ M$, although these runs were few because of their questionable significance. Ionic strength was adjusted to 2.0 *M* with $NaClO_4$ solution. The reaction was followed spectrophotometrically as before, both at 302 and at 515 nm; the experimental A_∞ reading at 302 nm was found to be reliable, as with the experiments at $I = 0.5\ M$, but the 515-nm end point showed a slight tendency to increase with time (probably because of oxidation of HN_3 by Co(III)) and A_∞ values calculated on the basis of the molar absorbancy index of $Co(NH_3)_5N_3^{2+}$, etc., were therefore used. The reaction was again found to be accurately first order in $[Co(NH_3)_5OH_2^{3+}]$, the first-order rate coefficients k_{an} of duplicate runs agreeing to within considerably better than 1.5%. These kinetic data are presented in Table II. (See also Figure 1.)

Ion-Pair Formation Constant Determinations.—A marked enhancement of apparent molar absorbancy in the region 300–400 nm was observed when solutions containing, respectively, N_3^-–HN_3 buffer and $Co(NH_3)_5OH_2^{3+}$ were mixed; no such effect was observed for HN_3 with $Co(NH_3)_5OH_2^{3+}$ in the absence of N_3^-, so the enhancement can be ascribed to ion-pair formation between N_3^- and $Co(NH_3)_5OH_2^{3+}$.

The magnitude of this enhancement was recorded at 23° for

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[11] J. I. Bryant and H. Rosenwasser, *J. Chem. Educ.*, **39**, 296 (1962).

[12] F. Basolo and R. G. Pearson, "Mechanisms of Inorganic Reactions," 2nd ed, John Wiley & Sons, Inc., New York, N. Y., 1967, p 32.

[13] Rubber fittings (*e.g.*, serum caps) were attacked by HN_3 and so could not be used.

[14] J. F. Endicott and M. Z. Hoffmann, *J. Am. Chem. Soc.*, **90**, 4740 (1968).

[15] R. K. Murmann, J. C. Sullivan, and R. C. Thompson, *Inorg. Chem.*, **7**, 1876 (1968).

Table II

Rate Coefficients for the Anation of $Co(NH_3)_5OH_2^{3+}$ by Azide Ion in Aqueous Perchlorate Media at 45° and $I = 2.00\ M$

$[N_3^-]$, *M*	$[HN_3]$, *M*	10^5k_{an}, sec^{-1}	$10^5k_{an}/[N_3^-]$, $M^{-1}\ sec^{-1}$
0.201	0.199	0.508, 0.497	2.50
0.251	0.249	0.624, 0.629	2.49
0.305	0.895	0.714	2.34
0.304	0.596	0.717	2.36
0.302	0.298	0.723	2.39
0.503	0.497	1.15, 1.15	2.29
0.604	0.596	1.34, 1.35	2.22
0.704	0.696	1.56	2.22
0.805	0.795	1.69, 1.73	2.13
0.906	0.894	1.95	2.15
1.006	0.994	2.14	2.13
(1.50)	(1.50)	(3.35, 3.35)	(2.23)

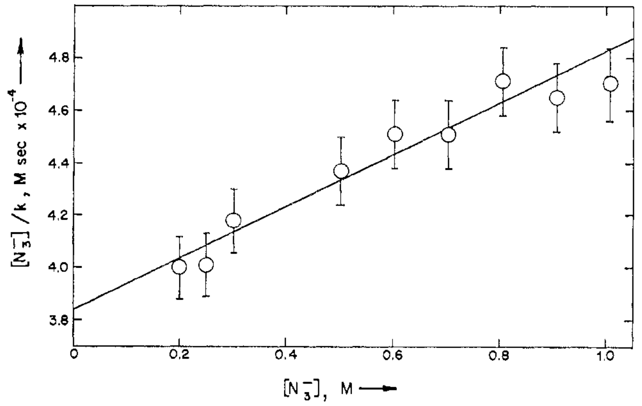

Figure 1.—Analysis of kinetics of anation of $Co(NH_3)_5OH_2^{3+}$ by N_3^- at 45° and $I = 2.0\ M$, assuming an ion-pairing preequilibrium (eq 2 and 5 of text). Plot of $[N_3^-]/k_{an}$ *vs.* $[N_3^-]$, allowing ±3% uncertainty in k_{an}.

solutions of ionic strength $I = 3.6\ M$. These solutions were prepared by mixing 1.0-ml aliquots of a solution, $1.0 \times 10^{-3}\ M$ in $[Co(NH_3)_5OH_2](ClO_4)_3$ and 0.495 *M* in $HClO_4$, with *n* ml of 4.0 *M* aqueous NaN_3 and $(9 - n)$ ml of 4.0 *M* $NaClO_4$ solution; "blanks" were prepared similarly, but without the Co(III) complex. The excess optical absorbances *A* of the mixtures over the blanks were measured at 320, 330, and 340 nm using 10-mm cells, and the enhancement δ of optical density was found by subtracting from *A* the optical density of equimolar $[Co(NH_3)_5OH_2](ClO_4)_3$ solutions in dilute $HClO_4$. The data so obtained were interpreted as explained below. Data for solutions of $I = 0.5\ M$ were also obtained, in an analogous way, but the enhancements of optical density were in general too small (average $A \approx 0.1$ or less) and therefore too inaccurate to justify detailed numerical analysis.

Results

The data of Table II show that the azide ion anation of $Co(NH_3)_5OH_2^{3+}$ is nearly, but not exactly, first order in $[N_3^-]$ over the concentration range 0.2–1.0 *M;* the deviation from first-order dependence of $[N_3^-]$ is small at low (<0.5 *M*) concentrations of azide. Consequently the data of Table I, for which $I = 0.5\ M$ and $0.1 \leqslant [N_3^-] \leqslant 0.4\ M$, can best be handled in terms of *specific* rate constants $k' = k_{an}/[N_3^-]$, which can be seen to be essentially constant within the limits imposed by the experimental error (which may be as much as ±3% in the case of the faster reactions). It can also be seen from Table I, and those experiments of Table II for which $[N_3^-] \approx 0.3\ M$, that there is no marked dependence of k' upon either $[HN_3]$ or $[H^+]$, within the ranges of these variables covered by the experiments. We may therefore conclude that the only important transition-state stoichiometry is $\{Co(NH_3)_5(H_2O)_xN_3^{2+}\}^*$, although the exact distribution of the constituent atoms (particularly the protons) within the transition state remains undefined. There is also some uncertainty concerning the number *x* of water molecules specifically involved in the transition state.

The average k' values of Table I give an excellent Arrhenius plot (log k' *vs.* $1/T$°K) such that the activation energy $E_a = 27.4$ kcal mol^{-1}. Alternatively, in terms of transition-state theory, $\Delta H^* = 26.87$ kcal mol^{-1} and $\Delta S^* = +5.2$ cal $deg^{-1}\ mol^{-1}$; the corresponding data for the reverse (aquation) reaction[1,2] are 33.4 kcal mol^{-1} and +13.5 cal $deg^{-1}\ mol^{-1}$, so that the formation of $Co(NH_3)_5N_3^{2+}$ is exothermic, with average $\Delta H° = -6.5$ kcal mol^{-1} over the temperature range studied. Assuming ΔC_p^* to be negligible for the anation reaction, we obtain by extrapolation a value of $k' = 1.74 \times 10^{-6}\ M^{-1}\ sec^{-1}$ at 25° and $I = 0.5$, and so, using Lalor and Moelwyn-Hughes' value[2] of $k_{aq} = 2.1 \times 10^{-9}\ sec^{-1}$ at 25°, we find the "stability constant" *Q* to be $8.3 \times 10^2\ M^{-1}$ at 25° and $I = 0.5\ M$.

The above considerations have been based on the assumption that the specific rate constant k' can be regarded as being independent of $[N_3^-]$ up to $[N_3^-] \approx 0.4\ M;$ this is reasonable enough, in view of the experimental uncertainty, but the data of Table II show clearly that k' actually decreases progressively as $[N_3^-]$ is increased from 0.2 to 1.0 *M*, and, in fact, the better data of Table I show this trend to a limited degree. This effect can be ascribed to an ion-pairing preequilibrium[4] (eq 2) with an equilibrium quotient $Q_{IP} = [Co(NH_3)_5OH_2^{3+},N_3^-]/[Co(NH_3)_5OH_2^{3+}][N_3^-]$, preceding the replacement of the aquo ligand by N_3^- (this being governed by the first-order rate coefficient *k*). If this interpretation is correct (and the reality of ion pairing has been demonstrated by the optical absorption enhancement experiments), then[4]

$$k_{an} = \frac{kQ_{IP}[N_3^-]}{1 + Q_{IP}[N_3^-]} \qquad (5)$$

The deviation of $k_{an}/[N_3^-]$ from constancy is quite small, even over wide ranges of $[N_3^-]$, and so Q_{IP} must be quite small ($<1\ M^{-1}$); by the same token, it is difficult to determine Q_{IP} with much accuracy from the kinetic data. Nevertheless, by plotting $[N_3^-]/k_{an}$ against $[N_3^-]$, with due allowance for a possible 3% uncertainty in k_{an}, we obtain essentially a straight line (Figure 1) of slope 0.99×10^4 sec ($=k^{-1}$) and intercept 3.84×10^4 ($=k/Q_{IP}$), so that $k = 1.01 \times 10^{-4}\ sec^{-1}$ and $Q_{IP} = 0.26\ M^{-1}$ at 45° and $I = 2.0\ M$. Alternatively, if k_{an}^{-1} is plotted against $[N_3^-]^{-1}$, as in Figure 2, we again find from the intercept that $k \approx 1.1 \times 10^{-4}\ sec^{-1}$—certainly, even the most distorted extrapolation would require that *k* be very markedly greater than the value of $2 \times 10^{-5}\ sec^{-1}$ which is typical[4] for the reactions of $Co(NH_3)_5OH_2^{3+}$ with Cl^-, NCS^-, or SO_4^{2-} at 45°.

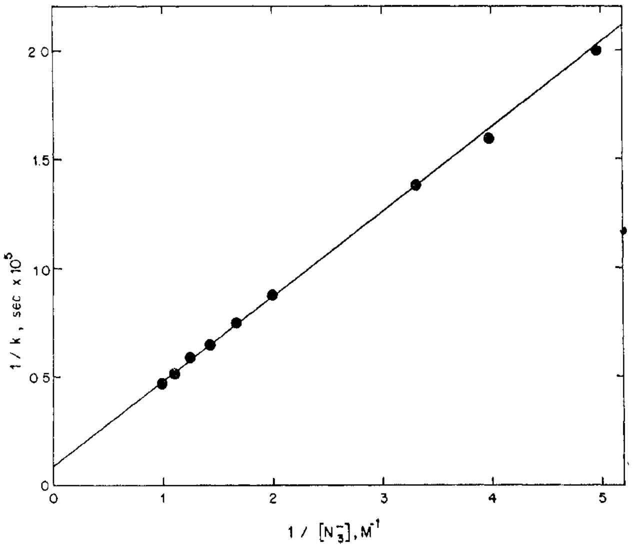

Figure 2.—Analysis of kinetics of anation of $Co(NH_3)_5OH_2^{3+}$ by N_3^- at 45° and $I = 2.0\ M$, assuming an ion-pairing preequilibrium (eq 2 and 5 of text). Plot of $1/k_{an}$ *vs.* $1/[N_3^-]$.

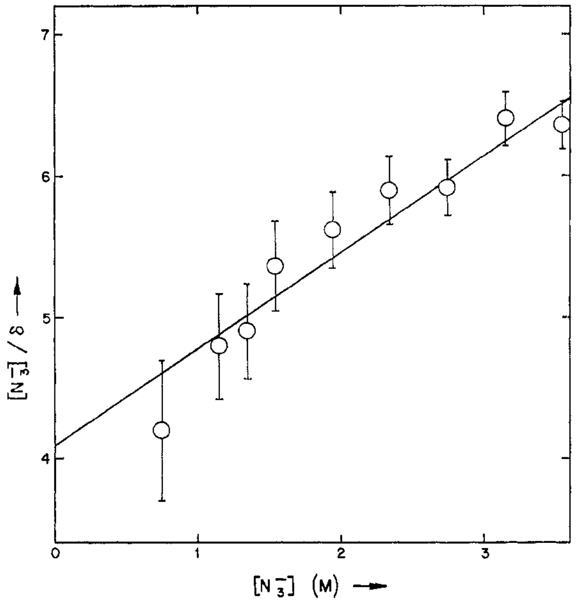

Figure 3.—Interpretation of enhancement δ of optical density in terms of $[Co(NH_3)_5OH_2^{3+},N_3^-]$ ion-pair formation at 23° and $I = 3.6$ (eq 6 of text). Uncertainty limits correspond to ±0.02 in δ.

Kinetic data obtained at $[N_3^-] > 1.0\ M$ (*i.e.*, experiments in which supplementary HN_3 solution had to be added) did not fit the straight line of Figure 1 very well; this is to be expected, since in these experiments the medium changes from predominantly perchlorate to predominantly azide beyond $[N_3^-] \approx 1.0\ M$; furthermore, ion triplet formation, the reduction of Co(III) to Co(II) by HN_3, and the possibility of interaction with trace impurities in the HN_3 and NaN_3 all become increasingly important as sources of error at high $[N_3^-]$.

In view of the uncertainty in assigning a Q_{IP} value by this method, a direct spectrophotometric determination of this quantity was attempted, using the enhancement δ of optical absorbance in the near-ultraviolet spectrum due to ion-pair formation, as described above. In principle,[16] if no ion triplets are formed, then

$$[N_3^-]/\delta = (1/Q_{IP}\epsilon C) + ([N_3^-]/\epsilon C) \qquad (6)$$

where ε is the difference in molar absorbancy index between the ion pair and the $Co(NH_3)_5OH_2^{3+}$ ion, and C is the *total* Co(III) concentration ($C << [N_3^-]$).

A plot of $[N_3^-]/\delta$ *vs.* $[N_3^-]$ at constant C should give a straight line of intercept $(Q_{IP}\epsilon C)^{-1}$ and slope $(\epsilon C)^{-1}$, whence Q_{IP} can be found. Values of Q_{IP} at $I = 2.0\ M$ and 45° cannot be obtained in this way, because of the rapidity of the increase of optical density through $Co(NH_3)_5N_3^{2+}$ formation; conversely, attempts to evaluate Q_{IP} at 25° and $I = 0.5\ M$ were unsatisfactory (see Experimental Section) but suggested $Q_{IP} \approx 0.1$–$0.2\ M^{-1}$ under these conditions. However, data obtained at 25° and $I = 3.6\ M$ indicated $Q_{IP} = 0.18 \pm 0.05\ M^{-1}$; Figure 3 shows a plot of one of three such sets of data (in this case, $Q_{IP} \approx 0.17\ M^{-1}$). With due allowance for ionic strength and temperature differences,[17] this lends credibility to the value $Q_{IP} = 0.26\ M^{-1}$ obtained kinetically at 45° and $I = 2.0\ M$ and hence ultimately shows that our assumption of the mechanism of eq 2 is justified. It is reassuring to note that Langford and Muir[4] find $Q_{IP} \approx 0.4$ for the rather similar system $Co(NH_3)_5OH_2^{3+} + NCS^-$.

Discussion

The simplest interpretation of the above kinetic data would be that the kinetics and mechanism of anation of $Co(NH_3)_5OH_2^{3+}$ by X^{n-} are much the same when $X^{n-} = N_3^-$ ($k' = 1.74 \times 10^{-6}\ M^{-1}\ sec^{-1}$ at 25°, $I = 0.5\ M$) as when $X^{n-} = Cl^-$, Br^-, NCS^-, NO_3^-, NH_3, or $H_2PO_4^-$ ($1.3 \times 10^{-6} \leqslant k' \leqslant 2.5 \times 10^{-6}\ M^{-1}\ sec^{-1}$ under similar conditions[18]), and it can therefore be stated with justification that the dissociation of the aquo ligand is the predominant rate-determining factor in all of these anation reactions. However, the data of Table II seem to require the more detailed treatment of Langford and Muir,[4] in accordance with eq 2 and 5, and we believe that the value $Q_{IP} = 0.26\ M^{-1}$ (45°, $I = 2.0\ M$), derived on the basis of eq 5, is meaningful, despite the lack of *direct* confirmation of this value from nonkinetic experiments. Accordingly, the rate constant k, which governs the conversion of the ion pair $\{Co(NH_3)_5OH_2^{3+}, N_3^-\}$ to the inner-sphere complex $Co(NH_3)_5N_3^{2+}$, can be taken as $1.0 \times 10^{-4}\ sec^{-1}$ (45°, $I = 2.0\ M$), a number which can be supported by Figure 2 without reference to a predetermined value of Q_{IP}.

A striking feature of the latter interpretation is that k for $X^{n-} = N_3^-$ is evidently some five times larger than is usual[4] for other X^{n-}. This discrepancy is perhaps not large in view of the uncertainties involved in estimating k and in comparing data obtained at various

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[16] F. J. C. Rossotti and H. Rossotti, "The Determination of Stability Constants," McGraw-Hill Book Co. Inc., New York, N. Y., 1961, Chapter 13.

[17] Coulombic anion–cation interactions can be expected to be somewhat endothermic and to increase with I at $I > 0.5\ M$; thus, Q_{IP} values at 45° and $I = 2.0\ M$ will be only a little different from those at 23° and $I = 3.6\ M$, since differences in these two factors will tend to be mutually compensatory.

[18] Reference 12, p 203.

ionic strengths (though k is not likely to be significantly dependent upon ionic strength), but we consider it great enough to merit comment, especially since k (45°, I = 2.0 M) for $X^- = N_3^-$ is effectively equal to the rate coefficient for the exchange of the aquo ligand of free $Co(NH_3)_5OH_2^{3+}$ with oxygen-18-labeled bulk water solvent[19] (which seems to be an "SN1" or dissociatively activated process[19]), namely, 1.0×10^{-4} sec^{-1} at 45° and $I \approx 0.6$ M. If one assumes (not unreasonably) that the outer-sphere association of N_3^- with $Co(NH_3)_5OH_2^{3+}$ does not appreciably affect the reactivity of the aquo ligand toward exchange with the solvent, then the evidence strongly suggests a mechanism in which the independent dissociation of the aquo ligand in the ion pair is invariably followed at once by the entry of the azide to take its place. This is in accordance with the "dissociative interchange" ("SN1" or "I_d") mechanism which seems to be operative in other typical $Co(NH_3)_5OH_2^{3+}$–X^{n-} substitution reactions,[4] except that usually only one aquo dissociation in five (on the average) results in the entry of X^{n-} from the second coordination sphere, whereas, in the case of $X^{n-} = N_3^-$, *all* aquo dissociations must result in azide entry.

This strongly suggests that the N_3^- ion is somehow specifically associated with the aquo group so that N_3^- is ideally sited for attachment to cobalt as the OH_2 ligand leaves. Hydrogen bonding of the basic azide ion through the aquo protons (which are much more acidic than the ammine protons) provides an obvious mechanism for this association. This model parallels that postulated previously[1] for the aquation reaction, and so the two hypotheses are self-consistent in this respect.

The stoichiometry of the transition state as required by our data does not exclude the possibility that the reacting species are HN_3 and $Co(NH_3)_5OH^{2+}$; indeed, we consider[1] that the distribution of charge *in the transition state* for aquation (and hence, by the principle of microscopic reversibility, for anation too) approximates to HN_3 generation rather than N_3^- release. It does not follow, however, that molecular HN_3 as such survives beyond the transition state of aquation and escapes from the solvent cage; the reverse path, then, need not necessarily begin with the attack of HN_3 on a conjugate base species in order to reach this same transition state.

It is perhaps relevant to note that the reduction of aqueous $Co(H_2O)_6^{3+}$ by HN_3 is believed[15] to involve the attack of HN_3 on $Co(H_2O)_5OH^{2+}$. However, a mechanism of this type would require associative activation ("SN2" attack) by HN_3 in the pentaammine case, since the rate of unassisted dissociation of the –OH ligand is much less than that of the aquo group[18] (a restriction which does not apply in the case of the relatively labile $Co(H_2O)_5OH^{2+}$ ion); this mechanism is improbable, since we find that the rate of reaction of HN_3 with $Co(NH_3)_5OH_2^{3+}$ is negligible despite the greater positive charge on the complex and the correspondingly greater tendency (if any) to associative activation by nucleophiles.

Furthermore, the very close correspondence between the rates of aquo dissociation from $Co(NH_3)_5OH_2^{3+}$ and azide entry from the ion pair seems to demand that aquo dissociation be the activating factor, while the very existence of the decreasing trend in k' as $[N_3^-]$ is increased points to $Co(NH_3)_5OH_2^{3+}$ and N_3^- as the reacting species through their ion pair, rather than HN_3 and the conjugate base. Finally, the dissociative mechanism proposed is readily related to that generally accepted for the formation of most other acidopentaamminecobalt(III) complexes, in accordance with the implication of Figure 4 that the azido complex is not *radically* different mechanistically from its analogs.

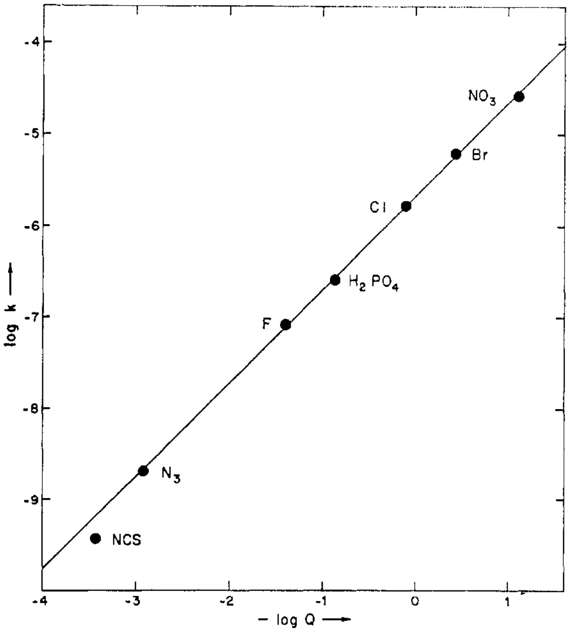

Figure 4.—Free energy of activation as a function of free energy of reaction for the aquation of $Co(NH_3)_5X^{2+}$ at 25° and I = 0.5 M. Plot of log k_{aq} *vs.* $-\log$ (stability constant). Data from sources indicated in ref 20.

Figure 4 is an extension of Langford's[5] linear relationship between log k_{aq} and $-\log Q$ for the series $Co(NH_3)_5X^{2+}$; it will be seen that the azido complex correlates well in this LFER and that the slope is 1.0 as before.[5,20] This tells us that the mechanism of aquation of the azido complex is almost certainly nearly the same *electronically* as for the others. This is in accordance with our assertion[1] that the abnormally high ΔS^* associated with $Co(NH_3)_5N_3^{2+}$ aquation originates primarily in a much lower degree of electrostriction of solvent in this transition state as compared with others, because, according to Tobe,[21] the contribution of solvent electrostriction to the free energy ΔF^* of activation (*i.e.*, to log k_{aq}) is essentially zero, though electrostric-

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(19) H. R. Hunt and H. Taube, *J. Am. Chem. Soc.*, **80**, 2642 (1958).

(20) The values of k_{aq} and Q are as given in ref 12, pp 164–165, with the exceptions of the azido complex (this work) and the thiocyanato complex, for which we calculate $k_{aq} = 3.7 \times 10^{-10}$ sec^{-1} (from data of D. L. Gay and G. C. Lalor, *J. Chem. Soc.*, *A*, 1179 (1966)) and $Q = 2.7 \times 10^3$ M^{-1} (from data of J. W. Moore and R. G. Pearson, *Inorg. Chem.*, **3**, 1334 (1964)) at 25° and I = 0.5 M.

(21) M. E. Baldwin, S. C. Chan, and M. L. Tobe, *J. Chem. Soc.*, 4637 (1961).

tion of solvent will have marked effects on ΔH^* and ΔS^*. Conversely, the fact that $Co(NH_3)_5N_3{}^{2+}$ and $Cr(H_2O)_5F^{2+}$ correlate in their respective LFER's for aquation, despite anomalously large ΔH^* and ΔS^* values,[6] lends further support to the argument[21] that ΔF^* can be expected to reflect electronic trends more closely than does ΔH^*.

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Photolysis of Oxalatoammine Complexes of Cobalt(III) in Aqueous Solution[1]

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Three mixed oxalatoamminecobalt(III) complexes, $[Co(NH_3)_5C_2O_4H]Cl_2$, $[Co(NH_3)_4C_2O_4]Cl$, and $K[Co(NH_3)_2(C_2O_4)_2]\cdot H_2O$, have been found to undergo photoredox decomposition when irradiated in the near-ultraviolet spectrum or part of the visible spectrum. The photolysis products were Co(II), NH_3, CO_2, and $C_2O_4{}^{2-}$. The photochemical quantum yield was wavelength dependent and varied gradually with the number of oxalate groups and O–Co coordinative sites. The over-all mechanism is discussed.

Hexamine complexes of Co(III) are known to be unreactive when irradiated in aqueous solution at wavelengths corresponding to ${}^1A_{1g} \rightarrow {}^1T_{1g}$ or ${}^1A_{1g} \rightarrow {}^1T_{2g}$ transitions. Photochemical quantum yields of less than 10^{-3} have been reported for $Co(NH_3)_6{}^{3+}$ and $Co[H_2N(CH_2)_{2-4}NH_2]_3{}^{3+}$ under irradiation in visible and near-ultraviolet spectra around λ_{max} of the d–d absorption bands.[3-8] The photosensitivity of the ammine complexes is enhanced by the replacement of an NH_3 group by a halide, $N_3{}^-$, $NO_2{}^-$, $RCOO^-$, or SCN^- group.[3,9] The oxalato complexes of many transition metals are among the most light-sensitive complexes known. Tris(oxalato)cobalt(III) has been reported to undergo photoredox decompostion efficiently in aqueous solutions.[10-12] Quantum yields between 0.12 and 0.73 were published for $Co(C_2O_4)_3{}^{3-}$ on irradiation with light between 313 and 435 mμ.[13,14] Presently we want to report on the photochemical reactions of oxalatoamminecobalt(III) complexes in which the ratio of $C_2O_4{}^{2-}$ and NH_3 ligands is progressively changed. The following complexes have been photolyzed in aqueous solutions: $[Co(NH_3)_5C_2O_4H]Cl_2$, $[Co(NH_3)_4C_2O_4]Cl$, and $K[Co(NH_3)_2(C_2O_4)_2]\cdot H_2O$. The photochemical quantum yield was determined actinometrically at three different excitation wavelengths in the visible and near-ultraviolet regions of the spectrum. The chemical conversion was followed spectrophotometrically and the influence of the pH on the over-all reaction was considered.

Experimental Section

Synthesis of Complexes.—The three complexes were prepared by procedures previously described in the literature.[15,16] Only the violet isomer of potassium bis(oxalato)diamminecobaltate(III) monohydrate has been used in the present work, rather than the blue isomer which is relatively unstable in aqueous solution. The complexes were repeatedly recrystallized and characterized by comparison with reported spectroscopic properties.

Apparatus and Procedures.—Either a water-cooled 1000-W AH-6 mercury-arc lamp (high pressure) or a Hanovia 450-W arc source was used for irradiation except for quantum yield measurements in which a 125-W medium-pressure Hg-arc lamp (PEK Laboratories) was coupled with a high-intensity Bausch and Lomb monochromator. The irradiation wavelengths were selected by interposing appropriate glass and liquid filters between light source and sample cells or by the monochromator in actinometric measurements. Silica cells (1-cm) were used and absorption spectra were recorded on a Cary Model 15 spectrophotometer.

For preparative scale and product isolation experiments, the 450-W Hanovia arc source was used in conjunction with the immersion-well photochemical reactor in which approximately 225 ml of solution surrounded the water-cooled light source.

The ferric oxalate actinometer of Hatchard and Parker[17] was used to measure light intensities and photochemical quantum yields.

To follow the chemical conversion and to detect eventual dark reactions, 1-cm-path cells containing solutions of appropriate concentration were irradiated for different periods and the changes

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[1] Taken in part from the dissertation submitted by H. W. to the Graduate School of The George Washington University in partial fulfillment for the degree of Doctor of Philosophy.

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