The Hydrolysis of Certain Dinitro Complexes of Cobalt(III) in Concentrated Acid Solutions

Don G. Lambert[1] **and John G. Mason**[2]

Contribution from the Department of Chemistry, Virginia Polytechnic Institute, Blacksburg, Virginia. *Received August 2, 1965*

Abstract: The first-order rate constant for hydrolysis was measured as a function of acid concentration at 25° in a series of cobalt(III) dinitro complexes containing the "inert" ligands ammonia, ethylenediamine, 1,3-diaminopropane, 2,2′-bipyridine, or 1,10-phenanthroline. At a constant acid concentration, the rate constant *decreased* by a factor of about 100 as the inert ligand was varied from ammonia to 1,10-phenanthroline. Values of the parameters *w* and *w** in Bunnett's equations are consistent with nucleophilic attack by water on the protonated complex as the rate-determining step in both perchloric and hydrochloric acids.

The hydrolysis of *trans*-$[Co(en)_2(NO_2)_2]^+$ in various concentrated acid solutions has been examined in considerable detail.[3] From the values of *w* and *w** in Bunnett's equations,[4] nucleophilic attack by water on the protonated complex was postulated as the rate-determining step in all acids. In the present study, rate constants were obtained as a function of acid concentration for five *trans*-dinitro complexes containing inert ligands as diverse as ammonia and 1,10-phenanthroline.

Experimental Section

Preparation of Compounds. All chemicals used in the preparations were reagent grade except 1,3-diaminopropane. Complexes were dried overnight at 55° *in vacuo* before analysis but were used in rate studies after recrystallizing, washing with ethanol, then ether, and air drying. Analyses were performed by Galbraith Laboratories, Inc., Knoxville, Tenn.

All *trans*-$[Co(AA)_2(NO_2)_2]NO_3$ compounds were made by a light modification of the method Holtzclaw, Sheetz, and McCarty[5] (HSM) used to prepare *trans*-$[Co(en)_2(NO_2)_2]NO_3$. In the HSM procedure, a solution of 2 moles of diamine partly neutralized with 1.2 moles of nitric acid is added to a solution of 1 mole of cobalt(II) nitrate and 2.3 moles of sodium nitrite. Air is bubbled through the solution at room temperature until precipitation is complete; then the product is recrystallized from boiling water.

trans-Dinitrobis(1,3-diaminopropane)cobalt(III) nitrate, *trans*-$[Co(tn)_2(NO_2)_2]NO_3$, was made by the HSM procedure from 67 ml (1 mole) of Eastman Practical Grade 1,3-diaminopropane which had been freshly distilled. The product was air-oxidized for 3 hr and twice quickly recrystallized from hot water. *Anal.* Calcd for $CoC_6H_{20}N_7O_7$: Co, 16.3; C, 20.0; H, 5.58; N, 27.2. Found: Co, 16.2; C, 20.1; H, 5.60; N, 26.9.

trans-Dinitrobis(2,2′-bipyridine)cobalt(III) nitrate, *trans*-$[Co(dipy)_2(NO_2)_2]NO_3$, was made by the HSM procedure from 5 g of bipyridine by boiling the solution during the 0.5-hr air oxidation and was recrystallized as usual. *Anal.* Calcd for $CoC_{20}H_{16}N_7O_7$: Co, 11.2; C, 45.7; H, 3.07; N, 18.7. Found: Co, 11.5; C, 45.5; H, 3.27; N, 18.5.

The preparation of *trans*-dinitrobis(1,10-phenanthroline)cobalt(III) nitrate, *trans*-$[Co(phen)_2(NO_2)_2]NO_3$, was attempted by the HSM procedure from 10 g of *o*-phenanthroline by boiling the solution during the hour of air oxidation and recrystallizing as usual. There is considerable question as to the structure of this product. The preponderance of evidence seems to point to a *cis* configuration rather than a *trans* as was initially assumed.

Ablov's method[6] was used to make $[Co(phen)_2Cl_2]Cl$ which was nitrosated *in situ* by addition of 2.5 moles of sodium nitrite. The dinitro product after recrystallization from water exhibited the same behavior as the HSM product when treated with concentrated hydrochloric acid, *i.e.*, rapid conversion to the *trans*-dichloro complex. Ablov assigned a *cis* configuration to his product.

Anal. Calcd for $CoC_{24}H_{16}N_7O_7 \cdot H_2O$: Co, 10.0; C, 48.7; H, 3.08; N, 16.6. Found: Co, 10.0; H, 48.7; H, 3.30; N, 16.6.

trans-Dinitrotetraamminecobalt(III) chloride, *trans*-$[Co(NH_3)_4(NO_2)_2]Cl$, was synthesized by a standard method[7] and twice recrystallized from water. *Anal.* Calcd for $CoN_6H_{12}O_4Cl$: Co, 23.1; H, 4.74; N, 32.9; Cl, 13.9. Found: Co, 23.1; H, 4.76; N, 33.1; Cl, 13.6.

trans-$[Co(en)_2(NO_2)(Cl)]NO_3$ and *trans*-$[Co(tn)_2(NO_2)(Cl)]NO_3$ were made by dissolving the respective dinitro complexes in concentrated hydrochloric acid at room temperature[8] and using the resulting solution. These complexes were not isolated as such.

cis-Dinitrotetraamminecobalt(III) nitrate, *cis*-$[Co(NH_3)_4(NO_2)_2]NO_3$, was made from the carbonate[8] and twice recrystallized from water. *Anal.* Calcd for $CoN_7H_{12}O_7$: Co, 21.0; H, 4.30; N, 34.9. Found: Co, 20.9; H, 4.58; N, 35.1.

cis-Chloronitrobis(ethylenediamine)cobalt(III) nitrate, *cis*-$[Co(en)_2(NO_2)(Cl)]NO_3$, was made by Werner's method;[8] the nitrate salt was obtained by adding potassium nitrate to a solution of the salt in concentrated hydrochloric acid. *Anal.* Calcd for $CoC_4H_{16}ClN_6O_5$: Co, 18.3; C, 14.9; H, 4.99; N, 26.1; Cl, 11.0. Found: Co, 18.6; C, 15.0; H, 5.02; N, 26.1; Cl, 10.8.

Kinetic Measurements. Rate constants were measured by techniques which have been described.[3] Experimental difficulties precluded measurement of the rate constants for hydrolysis of the phen and dipy complexes in dilute HCl.

Results

In Table I are listed data for the hydrolysis of five dinitro complexes in two acids at 25°. Variation of the rate constant with acid concentration could be described by Bunnett's equations[4a]

$$\log k_1 + H_0 = w \log a_w + C \tag{1}$$

$$\log k_1 - \log (H^+) = w^* \log a_w + D \tag{2}$$

where k_1 is the first-order rate constant at a given acid concentration, H_0 is the Hammett acidity function of that concentration, and a_w is the activity of water in the solution. The parameters *w* and *w** are the slopes, and *C* and *D* the intercepts, of plots of the left side of eq 1 or eq 2, respectively, *vs.* $\log a_w$. Water activities in Table I were obtained from Bunnett's compilation;[4a]

---

(1) Based on the dissertation presented by D. Lambert in partial fulfillment of the requirements for the degree of Doctor of Philosophy, Virginia Polytechnic Institute, 1965.

(2) To whom requests for reprints should be addressed.

(3) D. G. Lambert and J. G. Mason, *J. Am. Chem. Soc.*, **88**, 1633 (1966).

(4) (a) J. F. Bunnett, *ibid.*, **83**, 4956 (1961); (b) *ibid.*, **83**, 4968 (1961), (c) *ibid.*, **83**, 4973 (1961); (d) *ibid.*, **83**, 4983 (1961).

(5) H. F. Holtzclaw, D. P. Sheetz, and B. D. McCarty, *Inorg. Syn.*, **4**, 177 (1953).

(6) A. V. Ablov, *Russ. J. Inorg. Chem.*, **6**, 157 (1961).

(7) H. Blitz and W. Blitz, "Laboratory Methods of Inorganic Chemistry," 1st ed, John Wiley and Sons, Inc., New York, N. Y., 1909, p 178.

A. Werner, *Ann.*, **386**, 252 (1912).

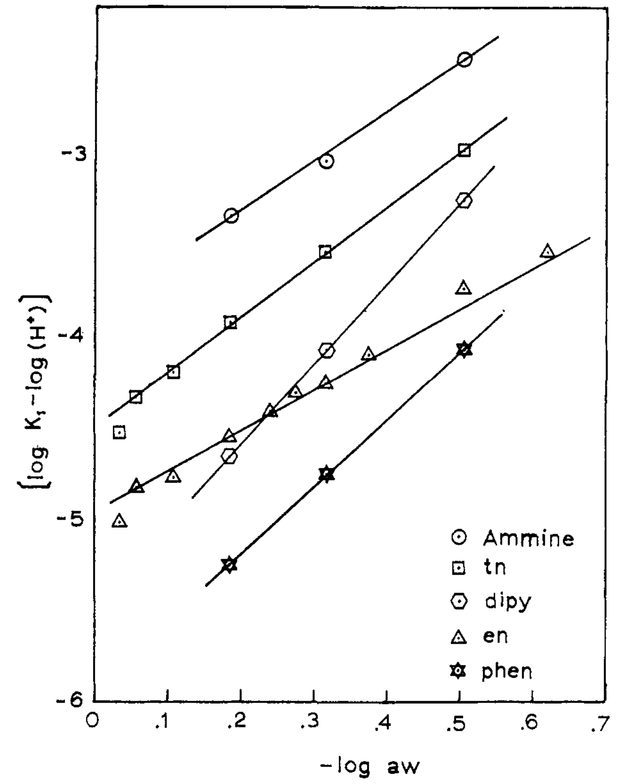

Figure 1. Hydrolysis of five *trans*-dinitro cobalt(III) complexes in $HClO_4$ at 25°: $\log k_1 - \log (H^+)$ *vs.* $\log a_w$.

rate constants for the ethylenediamine complex[9] are included for comparison.

Examination of Table I shows that the order of reactivity of the complexes is $NH_3 > tn > en > dipy > phen$, in 4.712 *M* perchloric acid.

Table I. Rate Variation for Change in (AA) in *trans*-$[Co(AA)_2(NO_2)_2]^+$ at 25°[a]

$HClO_4$, *M*	Inert ligand (AA)[b] 2NH₃	en	tn	dipy	phen[c]	$-\log a_w$
1.629	...	0.157	0.443	...	...	0.035
2.356	...	0.349	0.949	...	...	0.058
3.534	...	0.766	2.21	...	...	0.108
4.712	21.3	1.32	5.57	1.04	0.263	0.185
5.890	53.3	3.28	16.8	4.89	1.04	0.317
7.068	240	12.8	75.4	40.1	6.02	0.505

HCl, *M*	2NH₃	en	tn	$-\log a_w$
5.423	33.1	2.60	10.1	0.177
6.340	53.1	4.30	18.7	0.208
8.118	162	13.7	73.5	0.364

[a] First-order rate constant, $k_1 \times 10^4$ sec^{-1}. [b] Abbreviations are: en, ethylenediamine; tn, 1,3-diaminopropane; dipy, 2,2′-bipyridine; and phen, 1,10-phenanthroline. [c] Most probably *cis*.

Table II. *w* and *w** Values for Hydrolysis of *trans*-$[Co(AA)_2(NO_2)_2]^+$ in Two Acids

Inert ligand (AA)	Hydrochloric acid *w*	*w**	Perchloric acid *w*	*w**
2NH₃	2.1	−2.7	1.5	−2.8
en	2.4	−2.8	2.3	−2.4
tn	1.3	−3.5	1.3	−3.0
dipy	...	...	0.0	−4.4
phen[a]	...	...	1.0	−3.7

[a] Most probably *cis*.

Figure 1 shows a plot of the data for perchloric acid in Table I according to eq 2. Values of the parameters *w* and *w** for this data are presented in Table II. Note that in both acids, *w* varies from 0 to 3 in all cases, and *w** is less than −2. These values are consistent with nucleophilic participation of water in the rate-determining step.[4a]

Hydrolysis of Complexes in 11.88 *M* HCl. Rates of reaction for several different complexes are measured in 11.88 *M* hydrochloric acid at 25°. These data are listed in Table III. Examination of Table III shows that the *trans*/*cis* ratio is large for the $[Co(NH_3)_4(NO_2)_2]^+$ compounds, which is some support for an SN2 mechanism.[10]

Table III. Hydrolysis of Certain Complexes in 11.88 *M* HCl at 25°[a]

Complex Ion	*trans*	*cis*	*trans*/*cis*
$[Co(NH_3)_4(NO_2)_2]^+$	2300[b]	11.3	204
$[Co(en)_2(NO_2)_2]^+$	185	...	...
$[Co(tn)_2(NO_2)_2]^+$	2100[b]	...	...
$[Co(dipy)_2(NO_2)_2]^+$	56.3	...	...
$[Co(phen)_2(NO_2)_2]^+$	21.3	...	...
$[Co(en)_2(Cl)(NO_2)]^+$ [c]	0.0110	7.25	0.00151
$[Co(en)_2(Cl)(NO_2)]^+$ [d]	1.1	0.11	10
$[Co(tn)_2(Cl)(NO_2)]^+$ [c]	0.935	...	...

[a] First-order rate constant, $k_1 \times 10^4$ sec^{-1}. [b] Estimated from eq 2. [c] For removal of the nitro group. [d] For removal of the chloride in dilute acid solutions. From F. Basolo, B. D. Stone, J. G. Bergmann, and R. G. Pearson, *J. Am. Chem. Soc.*, **76**, 3079 (1954).

Discussion

Mechanism of Hydrolysis. The *w* and *w** parameters listed in Table II are consistent with a mechanism involving nucleophilic attack by water on the protonated complex as the rate-determining step. This mechanism has been discussed previously.[3]

Examination of Table III shows that the hydrolysis of the dinitro complexes is different from hydrolysis of the nitrochloro complexes. Possibly when chloride is the orienting ligand the nitro group is removed by an SN1 mechanism, and the change in the *trans*/*cis* ratio may support this conclusion. Caution is necessary, however, because the *trans* effect is not as yet clearly understood for octahedral complexes.[11]

Bunnett[4b] originally took +1.1 to +3.0 as the limits for *w* when water participated directly in the rate-determining step. In Table II *w* parameters of 0.0 and 1.0 are seen for the dipy and phen complexes, respectively. If the *w** parameter is[4c] $(t - s - n)$, where *s* is the hydration of the substrate, *n* is the hydration of the proton, and *t* is the hydration of the transition state, and the hydration number of the proton is

---

(9) D. G. Lambert, Ph.D. Thesis, Virginia Polytechnic Institute, 1965.

(10) C. K. Ingold, R. Nyholm, and M. Tobe, *Nature*, **187**, 477 (1960).

(11) F. Basolo and R. G. Pearson, *Advan. Inorg. Chem. Radiochem.*, **3**, 1 (1961).

4,[12] w^* is then $(t - s - 4)$. If both the substrate and the transition state have the same degree of hydration, $(t - s)$ is 0 and w^* is -4, close to the observed values of -3.7 and -4.4.

Bunnett's ideas[4] about acid hydrolysis reactions have proved very useful as empirical indicators of mechanism in the present study. Whether the theory[4c] relating w and w^* values exclusively to hydration changes is correct is not clear at this time. In fact many properties of concentrated acid solutions are related, so that separation of the various factors may be difficult. For example, in this work, fairly good correlations were found between the log k_1 and log a_{HCl}, where a_{HCl} is the activity of hydrochloric acid, for hydrolysis of *trans*-$[Co(en)_2(NO_2)_2]^+$ in this acid. Some caution is necessary in ascribing changes in rate to one factor exclusively.

The effect of the various ligands on the rate of hydrolysis as shown in Table I is not profound, which in itself is quite surprising considering the variety of ligands represented. Any detailed discussion of the relation between structural variation and mechanism, however, cannot be developed at this time.

In conclusion, it is heartening to find that, in general, these results support the mechanism postulated for the acid hydrolysis of *trans*-$[Co(en)_2(NO_2)_2]^+$ in a variety of acids and suggest that the Bunnett relations may be useful indicators of mechanism for reactions such as these. The extent to which these relations is valid can be established only by further work.

(12) K. E. Howlett, *Sci. Progr.*, **53**, 305, 1965, discusses this question.

Coordination Chain Reactions. II. The Ligand-Exchange Reaction of Tetraethylenepentaminenickel(II) and Ethylenediaminetetraacetatocuprate(II)

Dale W. Margerum and J. D. Carr

Contribution from the Department of Chemistry, Purdue University, Lafayette, Indiana. *Received December 6, 1965*

Abstract: The reaction between copper-EDTA and nickel-tetren to produce copper-tetren and nickel-EDTA is catalyzed by traces of either uncomplexed EDTA or tetren and is inhibited by traces of metal ion. A chain-reaction mechanism is proposed where the chain-propagating steps are the reaction of tetren with copper-EDTA and the reaction of EDTA with nickel-tetren. The pH profile of each chain-propagating step is established and used to explain the kinetic behavior in terms of the effect of pH, temperature, reversibility of a propagation step, switch of rate-determining steps, and pseudo-zero-order reactions.

The double ligand-exchange reaction between tetraethylenepentaminenickel(II)[1] and ethylenediaminetetraacetatocuprate(II), shown in eq 1, is thermodynamically favorable but is kinetically sluggish. It is

$$NiTe^{2+} + CuY^{2-} \longrightarrow CuTe^{2+} + NiY^{2-} \qquad (1)$$

catalyzed by traces of either tetren or EDTA and is inhibited by traces of metal ions. These are the same properties exhibited by the similar exchange between nickel-trien and copper-EDTA which was shown to proceed by a chain-reaction mechanism.[2] The present work continues the study of coordination chain reactions and the effect which an increase in the dentate number of the polyamine has on the kinetics. The chain-propagating steps (eq 2 and 3 with protons

$$Te + CuY^{2-} \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} CuTe^{2+} + Y^{4-} \qquad (2)$$

$$Y^{4-} + NiTe^{2+} \xrightarrow{k_3} NiY^{2-} + Te \qquad (3)$$

omitted) parallel those for trien but the values of the rate constants and their pH dependence are altered using tetren. The tetren chain reaction is of interest for several reasons. (1) The rate of dissociation of nickel-tetren (eq 4) is very much slower than that of nickel-

$$NiTe^{2+} \xrightarrow{k_d^{NiTe}} Ni^{2+} + Te \qquad (4)$$

trien,[3] and a higher chain length (rate of propagation/rate of initiation) is possible for the exchange reaction. The greater the chain length, the greater the possible sensitivity to traces of ligands or metals. (2) The nickel-tetren complex is more stable thermodynamically and can be used at lower pH than in the case with nickel-trien. (3) The kinetic effect of the reversibility of a chain-propagating step (eq 2) can be studied. Conditional stability constants[4] were calculated from the appropriate stability constants[5] for each complex from pH 4 to 13, and these constants are combined to

---

(1) Abbreviations used are: Te or tetren, tetraethylenepentamine; T or trien, triethylenetetramine; Y^{4-} or EDTA, ethylenediaminetetraacetate ion.

(2) D. C. Olson and D. W. Margerum, *J. Am. Chem. Soc.*, **85**, 297 (1963).

(3) D. W. Margerum, D. B. Rorabacher, and J. F. G. Clarke, Jr., *Inorg. Chem.*, **2**, 667 (1963).

(4) A. Ringbom, "Complexation in Analytical Chemistry," Interscience Publishers Inc., New York, N. Y., 1963, pp 38–56.

(5) (a) G. Schwarzenbach, R. Gut, and G. Anderegg, *Helv. Chim. Acta*, **37**, 937 (1954); (b) R. A. Cave and L. A. K. Stavely, *J. Chem. Soc.*, 4571 (1956); (c) P. Paoletti, A. Vacca, and I. Giusti, *Ric. Sci. Rend.*, **A33**, 523 (1963); (d) C. N. Reilley and J. H. Holloway, *J. Am. Chem. Soc.*, **80**, 2917 (1958).