able mechanistic model involves rupture of one ligand bond to give a symmetrical five-coordinate intermediate. A similar mechanism has been proposed for the stereochemical rearrangements of the dihalobis(β-diketonato)titanium complexes[5] and the coordination compounds of trivalent metals with unsymmetrical 1,3-diketones.[19]

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Some Decomposition Reactions of Diperoxotriamminechromium(IV)[1a]

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Decomposition of $Cr(NH_3)_3(O_2)_2$ in 1 *F* $HClO_4$ at 20–25° gives $Cr(NH_3)_3(OH_2)_3^{3+}$ (*ca.* 40%, probably the pure 1,2,3 (*cis*) isomer), $Cr(NH_3)_2(OH_2)_4^{3+}$ (*ca.* 35%, probably largely or wholly the *cis* isomer), $Cr(NH_3)(OH_2)_5^{3+}$ (*ca.* 15%), and $Cr(OH_2)_6^{3+}$ (*ca.* 10%). In 1 *F* NaOH at 102° the diperoxo compound decomposes *ca.* 95% *via* a path forming CrO_4^{2-}, NH_3, O_2, and H_2O (or possibly some H_2O_2); the other *ca.* 5% of reaction produces CrO_4^{2-} and a nitrogen-containing species which is neither NH_3 nor NO_2^- and which slowly reacts with the CrO_4^{2-} or which catalyzes the oxidation of H_2O by CrO_4^{2-}. Explosion of the diperoxo compound by sudden heating occurs *ca.* 90% *via* formation of Cr_2O_3, NH_3, and O_2; the other *ca.* 10% of reaction yields Cr_2O_3, N_2O, N_2, and H_2O.

Introduction

In recent papers[2–6] we have reported our studies of the decomposition of diperoxochromium(IV) amines in acid solutions so as to prepare new chromium(III) amine complexes. Here we report the decomposition of diperoxotriamminechromium(IV), $Cr(NH_3)_3(O_2)_2$, in 1 *F* perchloric acid to give a series of aquoamminechromium(III) complexes. We also describe observations on the decomposition of this diperoxo compound in 1 *F* sodium hydroxide at *ca.* 102° and by explosion in a closed vessel.

Experimental Section

Diperoxotriamminechromium(IV).—The method of Kauffman and Acero[7] was used to prepare some lots of this compound. For other lots, the less efficient but more convenient method of Wesch[8] was employed, giving lustrous black needles; yield, 7%. *Anal.* Calcd for $Cr(NH_3)_3(O_2)_2$: N, 25.0; Cr, 31.1. Found: N, 25.3; Cr, 31.0.

The diperoxo compound must be handled with care because it may explode on sudden heating or shock. When heated from 20–25° at 2°/min, the compound charred at *ca.* 300° but did not explode. When the heating rate was increased to 4°/min, the crystals exploded mildly at 255°, and with a 20°/min heating rate a more violent explosion occurred at *ca.* 120°. At 20–25°, the compound can apparently be kept without change for at least 1 year.

Decomposition in 1 *F* Perchloric Acid.—*Ca.* 0.2 g of $Cr(NH_3)_3(O_2)_2$ was dissolved cautiously in 50 ml of 1 *F* $HClO_4$ at 20–25°; effervescence occurred. *Ca.* 5 ml of an aqueous slurry of H^+ Dowex AG50W-X4 cation-exchange resin (200–400 mesh) was added to the pink solution and shaken gently for 5 min, by which time all color was adsorbed. The resin was removed, washed with two 25-ml portions of 1 *F* $HClO_4$, and then transferred to the top of a 25-cm × 1-cm diameter column of fresh resin. Elution at 20–25° with a solution 0.15 *F* in $Ca(ClO_4)_2$ and 0.15 *F* in $HClO_4$ at 1 ml/min (a low rate is essential for the separation) yielded four bands as follows.

Ca. 500 ml of eluent separated the lowest band and brought it to the bottom of the column. A further 100–150 ml eluted this band to give a grayish blue solution. To remove Ca^{2+} from this effluent, it was readsorbed on a 3-cm × 1-cm diameter column of H^+ Dowex AG50W-X8 resin (100–200 mesh) at 20–25°, the Ca^{2+} was eluted with 200 ml of 1 *F* $HClO_4$, and then the complex was eluted with 50 ml of 3 *F* $HClO_4$. The resulting solution was 1.3 m*M* in $Cr(OH_2)_6^{3+}$, identified as such by its visible absorption spectrum.[9] The hexaaquo complex constituted *ca.* 10% of the total chromium.

Ca. 100 ml of eluent brought the next band to the bottom of the column, and 100–150 ml more eluted the band as a pink-red solution. Removal of Ca^{2+} was effected as above, giving a solution 1.7 m*M* in $Cr(NH_3)(OH_2)_5^{3+}$, characterized by its visible absorption spectrum.[10] *Ca.* 15% of the total chromium was as this pentaaquo species.

The third band was brought down with *ca.* 100 ml of eluent and eluted as a pink effluent with an additional 100–150 ml of eluent. The Ca^{2+} was removed, giving a solution 2.0 m*M* in complex, with an N:Cr atom ratio of 1.95, in acceptable agreement with the formula $Cr(NH_3)_2(OH_2)_4^{3+}$. This diammine species constituted *ca.* 35% of the total chromium.

The last band was brought down and eluted in the same way. After removal of Ca^{2+}, a pink solution 3.7 m*M* in complex was obtained. The N:Cr atom ratio found for this effluent was 2.81, in acceptable agreement with the formula $Cr(NH_3)_3(OH_2)_3^{3+}$. *Ca.* 40% of the total chromium was in this form.

The decomposition and chromatographic separations were repeated several times with essentially the same results.

Decomposition in Hot 1 *F* Sodium Hydroxide.—In each of

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(2) D. A. House and C. S. Garner, *Inorg. Nucl. Chem. Letters*, **1**, 137 (1965).

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(8) A. Wesch, "Über Chromsäurederivate," Diss. Freiburg im Breisgau, Offenbach a. M., 1908, p 19.

(9) R. A. Plane and J. P. Hunt, *J. Am. Chem. Soc.*, **79**, 3343 (1957).

(10) M. Ardon and B. E. Mayer, *J. Chem. Soc.*, 2816 (1962).

several experiments, *ca.* 0.1 g of $Cr(NH_3)_3(O_2)_2$ was weighed into a vial, which was placed upright in the boiler flask of a Kjeldahl distillation apparatus; *ca.* 2 g of NaOH was put in the flask, and then 50 ml of water was added. Except in the experiments at 20–25° (where air was used as a carrier gas to remove NH_3), steam was passed into the solution until it boiled, by which time the vial had become immersed, the NaOH had dissolved, and the diperoxo compound had reacted with effervescence. Distillation into saturated boric acid solution was continued for 10 min; then the adsorbed NH_3 was titrated with standard HCl. The average yield of NH_3 was 2.83 ± 0.04 moles per formula weight of $Cr(NH_3)_3(O_2)_2$.

The decrease in oxidation equivalents in the alkaline decomposition was followed by acidifying with 1 *F* H_2SO_4 the residual solutions left in the Kjeldahl boiler flask, adding excess standard $Fe(NH_4)_2(SO_4)_2$, and back-titrating the excess with standard $K_2Cr_2O_7$, using barium diphenylaminesulfonate indicator.

Decomposition by Explosion.—In each of several experiments, *ca.* 0.2 g of $Cr(NH_3)_3(O_2)_2$ was put in a steel bomb, which was then evacuated to 0.1 torr and sealed. The base of the bomb was heated rapidly with a burner flame to explode the compound (in a test experiment with the bomb left unsealed, the noise accompanying the explosion verified that the heating conditions resulted in explosion). The explosion products consisted of a dark green solid and a gas. The solid, unaffected by fusion with Na_2O_2 or $Na_2S_2O_7$, is apparently a refractory form of Cr_2O_3, since its weight corresponded within 1% to one formula weight of Cr_2O_3 produced for each two formula weights of $Cr(NH_3)_3(O_2)_2$ exploded. The gas produced in the explosion was examined by injection into an AEI MS9 mass spectrometer, by recording its infrared absorption spectrum in a 10-cm cell with NaCl windows on a Perkin-Elmer Infracord Model 137 spectrometer in the 700–4000-cm^{-1} region, and by determining the average molecular weight by the gas density method.

Chemical Analyses.—Samples of $Cr(NH_3)_3(O_2)_2$ were analyzed for Cr by boiling weighed samples in alkaline peroxide to oxidize the Cr to CrO_4^{2-} and to decompose excess peroxide, then acidifying with 1 *F* H_2SO_4, adding excess standard $Fe(NH_4)_2(SO_4)_2$, and back-titrating the excess with standard $K_2Cr_2O_7$, using barium diphenylaminesulfonate indicator. The diperoxo compound was analyzed for N by a micro-Dumas method by the Microanalytical Department of the Department of Organic, Inorganic, and Theoretical Chemistry of the University of Cambridge.

Spectrophotometry.—Visible and near-ultraviolet spectra of aqueous solutions of the complexes obtained by chromatography of the solutions from decomposition in 1 *F* $HClO_4$ were recorded in 10-cm quartz cells with a Cary Model 15 spectrophotometer, using water in the matched reference cell.

Results and Discussion

Decomposition in 1 *F* Perchloric Acid.—Four complexes were isolated in pure form in aqueous solution by cation-exchange chromatography of solutions obtained by the decomposition of $Cr(NH_3)_3(O_2)_2$ in 1 *F* $HClO_4$ at 20–25°. The first and second species eluted in the chromatography were identified as hexaaquochromium(III) cation, $Cr(OH_2)_6^{3+}$, and pentaaquoamminechromium(III) cation, $Cr(NH_3)(OH_2)_5^{3+}$.

The third complex eluted was formulated as $Cr(NH_3)_2(OH_2)_4^{3+}$ on the basis of the N:Cr atom ratio (1.95) found for it and its elution behavior, which is compatible with a 3+ charge.[11] Three references[12-14] to "*cis*-$Cr(NH_3)_2(OH_2)_4^{3+}$" have been found in the literature, but in each case no convincing evidence was presented for such a species, and no claim was made for its isolation. The visible absorption spectrum of a complex described as *trans*-$Cr(NH_3)_2(OH_2)_4^{3+}$ has been reported;[12] the configuration assignment is uncertain since it was based solely on derivation of the complex from *trans*-$Cr(NH_3)_2(NCS)_4^{-}$. Comparison of the spectrum of our $Cr(NH_3)_2(OH_2)_4^{3+}$ with that of the alleged *trans*-$Cr(NH_3)_2(OH_2)_4^{3+}$ and of tetraaquoethylenediaminechromium(III) cation, $Cr(en)(OH_2)_4^{3+}$ [15] (see Table I), indicates considerable similarity among all three spectra. Since the N chromophores in $Cr(en)(OH_2)_4^{3+}$ are necessarily *cis* to one another, this spectral similarity suggests that our $Cr(NH_3)_2(OH_2)_4^{3+}$ is largely or wholly the *cis* isomer. Presumably only a small proportion could be the *trans* isomer, since no evidence of separation into isomeric fractions was noted in the chromatography, and from previous experience we would expect at least a partial separation if both isomers were present. The above spectral similarity may also mean that the alleged *trans*-$Cr(NH_3)_2(OH_2)_4^{3+}$ is largely the *cis* isomer, or possibly the *cis* and *trans* isomers may differ little in their visible absorption spectra, as suggested for other reasons in ref 13.

The fourth complex eluted was formulated as $Cr(NH_3)_3(OH_2)_3^{3+}$ on the basis of its N:Cr atom ratio (2.81) and its elution behavior. Although solids described as salts of $Cr(NH_3)_3(OH_2)_3^{3+}$ have been made by a variety of methods,[16-19] they apparently were not characterized beyond elemental analyses or examined spectrophotometrically, except for a salt made by Colmar and Schwartz[20] and $[Cr(NH_3)_3(OH_2)_3](ClO_4)_3$ synthesized by Edelson and Plane,[21] both salts (of unknown isomeric purity) having been made by the method of Werner.[18] The only other spectral information apparently reported on the triaquo complex is for a $Cr(NH_3)_3(OH_2)_3^{3+}$ species obtained by Schäffer and Andersen[14] by the action of $Hg(ClO_4)_2$ on $Cr(NH_3)_3Cl_3$ (obtained by the action of hydrochloric acid on a particular equilibrium solution they believed to contain mainly $(NH_3)_3Cr(OH)_3Cr(NH_3)_3^{3+}$); Schäffer and Andersen claim the spectrum is proof of a 1,2,3 (*cis*) configuration for their $Cr(NH_3)_3(OH_2)_3^{3+}$. The absorption spectra maxima and minima of these triaquo complexes are presented in Table I. The $Cr(NH_3)_3(OH_2)_3^{3+}$ spectra are all similar, resemble the spectrum of 1,2,3-$Cr(dien)(OH_2)_3^{3+}$,[22] and are significantly different from the spectrum of 1,2,6-$Cr(dien)(OH_2)_3^{3+}$ [22] (see Table I). Inasmuch as these two diethylenetriamine complexes have the same Cr–N and Cr–O chromophores

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(11) Deduction of the charge of the chromium cations from the chromatographic behavior is not directly possible, because of the large volumes of Ca^{2+} eluent. However, a known solution of $Cr(OH_2)_6^{3+}$ and $Cr(en)(OH_2)_4^{3+}$, subjected to essentially the same elution with Ca^{2+}, chromatographed similarly, with $Cr(OH_2)_6^{3+}$ eluted first. Moreover, all of the complexes formed when $Cr(NH_3)_3(O_2)_2$ was decomposed in 1 *F* $HClO_4$ were eluted with 50 ml of 3 *F* $HClO_4$, further supporting the 3+ charge assumed for the complexes.

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(13) J. Bjerrum and E. Jørgensen, *J. Inorg. Nucl. Chem.*, **8**, 313 (1958).

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(19) F. Frowein, *Z. Anorg. Allgem. Chem.*, **110**, 107 (1920).

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(21) M. R. Edelson and R. A. Plane, *Inorg. Chem.*, **3**, 231 (1964).

TABLE I

ABSORPTION MAXIMA AND MINIMA IN THE 14,000–31,000-CM^{-1} REGION OF SOME AQUOAMINECHROMIUM(III) COMPLEXES IN AQUEOUS SOLUTION AT 18–25°

Complex	Medium	$\tilde{\nu}$, cm^{-1}	a_M, M^{-1} cm^{-1} [a]
$Cr(NH_3)_2(OH_2)_4^{3+}$ [b]	3 F $HClO_4$	26,200 (max)	18.5
		22,700 (min)	5.3
		19,200 (max)	21.0
trans(?)-$Cr(NH_3)_2(OH_2)_4^{3+}$ [c,d]	0.5 F HNO_3	26,200 (max)	24
		22,200 (min)	9
		19,200 (max)	22
$Cr(en)(OH_2)_4^{3+}$ [e]	1–3 F $HClO_4$	26,000 (max)	24.3
		23,100 (min)	10.7
		19,500 (max)	41.7
		15,200 (min)	0.5
		15,000 (max)	1.4
1,2,3(?)-$Cr(NH_3)_3(OH_2)_3^{3+}$ [b]	3 F $HClO_4$	26,800 (max)	25.6
		23,400 (min)	8.0
		19,900 (max)	25.6
		14,700 (sh)	1
1,2,3(?)-$Cr(NH_3)_3(OH_2)_3^{3+}$ [d,f]	2 F $HClO_4$	26,700 (max)	22.2
		23,100 (min)	6.5
		19,300 (max)	34.5
$Cr(NH_3)_3(OH_2)_3^{3+}$ [g]	0.05 F $HClO_4$	26,500 (max)	25.9
		19,700 (max)	27.0
$Cr(NH_3)_3(OH_2)_3^{3+}$ [d,h]	H_2O?	19,600 (max)	27
1,2,3-$Cr(dien)(OH_2)_3^{3+}$ [i]	1–2 F $HClO_4$	26,700 (max)	33
		23,400 (min)	12
		19,600 (max)	66
1,2,6-$Cr(dien)(OH_2)_3^{3+}$ [i]	0.3 F $HClO_4$	25,600 (max)	45
		23,500 (min)	38
		20,200 (max)	90

[a] Molar absorbancy index (molar extinction coefficient ϵ), defined by $A = \log (I_0/I) = a_M cd$, where c is the molarity of absorbing complex and d is the optical path in centimeters. [b] This research. [c] Reference 12; a spectral graph given in ref 14 and labeled simply as the diammine is essentially the same. [d] Estimated from a spectral graph in the cited literature. [e] Reference 15. [f] Reference 14. [g] Reference 21. [h] Reference 20. [i] Reference 22.

as the triaquotriammine complex, this spectral similarity suggests that all of the $Cr(NH_3)_3(OH_2)_3^{3+}$ complexes of Table I are mainly the 1,2,3 isomer, but not necessarily isomerically pure. The $Cr(NH_3)_3(OH_2)_3^{3+}$ obtained by us from $Cr(NH_3)_3(O_2)_2$ is probably isomerically pure 1,2,3 isomer since no evidence for separation into isomers was found in our chromatography, and we would expect at least partial separation if both isomers were present.

In the $Cr(NH_3)_3(O_2)_2$ molecule, which in the crystal has a distorted pentagonal-bipyramidal configuration,[23] the N atoms are nearly at the 1,2,6 positions of an octahedron. Hence, if the geometric configuration is at least approximately preserved in the decomposition, we would expect the 1,2,6 isomer of $Cr(NH_3)_3(OH_2)_3^{3+}$ to be the dominant product of the decomposition in perchloric acid. Although $Cr(NH_3)_3(OH_2)_3^{3+}$ of unknown geometric configuration is a decomposition product, it accounts for only *ca.* 40% of the total chromium in the products. The remaining 60% is made up of what at first thought might be considered its aquation products, namely, $Cr(NH_3)_2(OH_2)_4^{3+}$, $Cr(NH_3)(OH_2)_5^{3+}$, and $Cr(OH_2)_6^{3+}$. However, the rates of aquation of $Cr(NH_3)_3(OH_2)_3^{3+}$, $Cr(NH_3)_2(OH_2)_4^{3+}$, and $Cr(NH_3)(OH_2)_5^{3+}$ are too low under the conditions involved for the tetraaquo, pentaaquo, and hexaaquo products to have been formed by such aquation. We believe their formation must instead arise as a result of decomposition, probably successive aquation followed by reduction, of a relatively short-lived intermediate, such as a hypothetical Cr(IV) complex, $Cr(NH_3)_3(OH_2)_3^{4+}$.

The stoichiometry of $Cr(NH_3)_3(O_2)_2$ decomposition in 1 F $HClO_4$ was studied only with regard to the identity of the chromium species produced. No chromium(VI) species were found.

Decomposition in 1 F Sodium Hydroxide.—The decomposition of $Cr(NH_3)_3(O_2)_2$ in 1 F NaOH at *ca.* 102° is nonstoichiometric. Although 1.01 ± 0.01 mol of CrO_4^{2-} is initially formed per formula weight of $Cr(NH_3)_3(O_2)_2$ decomposed, only 2.83 ± 0.04 mol of NH_3 is found at 10-min or longer reaction times (technical problems prevent determination of the NH_3 liberated at shorter reaction times). Moreover, the total oxidizing power of the reaction solution (based on equivalents of Fe^{2+} oxidized per formula weight of $Cr(NH_3)_3(O_2)_2$ decomposed) decreases smoothly with time (see Table II) from the initial stoichiometric value of 3.0 to a value of 2.62 (apparently not far from an asymptotic value) at 90 min, although all of the NH_3 liberated has been removed from the reaction solution within the first 10 min. Control experiments showed no loss of CrO_4^{2-} (*ca.* 0.01 F) on boiling for 2 hr with 2 F NaOH when the solution was also: (a) *ca.* 0.03 F in NH_3, (b) *ca.* 0.2 F in H_2O_2, or (c) *ca.* 0.1 F in $NaNO_2$.

TABLE II

LOSS OF OXIDATION EQUIVALENTS PER FORMULA WEIGHT OF $Cr(NH_3)_3(O_2)_2$ IN A SOLUTION OF $Cr(NH_3)_3(O_2)_2$ DECOMPOSED IN 1 F NaOH

Temp, °C	Time, min	No. of oxidn equiv
102	2	3.04
102	20	2.89
102	30	2.85
102	45	2.75
102	60	2.67
102	90	2.62
102[a]	20	3.03
~22	1200	2.62

[a] NaOH omitted.

Thus, there appear to be at least two fast reactions associated with the decomposition of $Cr(NH_3)_3(O_2)_2$ itself, followed by at least one slow reaction involving CrO_4^{2-} and some product of the $Cr(NH_3)_3(O_2)_2$ decomposition. Of the fast reactions, *ca.* 95% of the decomposition probably occurs by the reaction

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(22) Originally a 1,2,3 configuration was tentatively assigned to a pink $Cr(dien)(OH_2)_3^{3+}$ complex made by decomposing $[Cr(dien)(O_2)_2]\cdot H_2O$ in 1 F $HClO_4$.[3] Subsequently, purple 1,2,6-$Cr(dien)Cl_3$ and green 1,2,3-$Cr(dien)Cl_3$ were synthesized by D. A. House, *Inorg. Nucl. Chem. Letters*, **3**, 67 (1967), and treated in 1 F $HClO_4$ with $Hg(ClO_4)_2$ to prepare what were thought to be 1,2,6- and 1,2,3-$Cr(dien)(OH_2)_3^{3+}$, respectively, and their visible absorption spectra were cited as such in ref 4. Recent unpublished experiments of D. K. Lin and C. S. Garner have supported the latter assignment but have shown that the supposed 1,2,6-$Cr(dien)(OH_2)_3^{3+}$ is actually mainly its aquation product, $Cr(dienH)(OH_2)_4^{4+}$. Subsequent unpublished experiments of D. A. House, confirmed in our laboratory, show that 1,2,6-$Cr(dien)(OH_2)_3^{3+}$ is relatively labile and that it can be made by base hydrolysis of 1,2,6-$Cr(dien)Cl_3$, followed by acidification. It is this spectrum which is given in Table I for 1,2,6-$Cr(dien)(OH_2)_3^{3+}$. Dr. House informs us that a structure determination of green $Cr(dien)Cl_3$ crystals nearing completion in the X-Ray Laboratory of the University of Canterbury, Christchurch, New Zealand, confirms the 1,2,3 configuration of the trichloro compound and thus strongly supports the 1,2,3 configuration of the triaquo complex obtained from it.

(23) R. Stomberg, *Arkiv Kemi*, **22**, 49 (1963).

$$Cr(NH_3)_3(O_2)_2 + 2OH^- = CrO_4^{2-} + 3NH_3 + H_2O + {}^1/_2O_2 \quad (1)$$

with probably only a small contribution if any from the alternative reaction

$$Cr(NH_3)_3(O_2)_2 + 2OH^- = CrO_4^{2-} + 3NH_3 + H_2O_2 \quad (2)$$

since the latter does not fully account for the following observations: (a) considerable gas is evolved in the decomposition of $Cr(NH_3)_3(O_2)_2$ either at ~22 or 102°; (b) Table II shows a slow loss of oxidizing power rather than the rapid initial loss expected if H_2O_2 were rapidly formed with subsequent rapid reduction of some CrO_4^{2-} *via* the reaction

$$Cr_2O_7^{2-} + 3H_2O_2 + 8H^+ = 2Cr^{3+} + 7H_2O + 3O_2 \quad (3)$$

on acidification for the Fe^{2+} titration;[24] (c) no visual evidence of formation of dark peroxychromates is observed upon acidification of any of the solutions of Table II. The additional *ca.* 5% of fast reaction associated with the $Cr(NH_3)_3(O_2)_2$ decomposition itself is one in which CrO_4^{2-} and an N-containing species other than NH_3 is formed. This N-containing species (0.17 ± 0.04 g-atom of N per formula weight of $Cr(NH_3)_3(O_2)_2$ decomposed) probably is slowly oxidized by the CrO_4^{2-}, thus accounting for the gradual loss of oxidizing power up to a maximum of perhaps 0.5 oxidation equiv (*ca.* 0.2 mol) of CrO_4^{2-} lost. Alternatively, this N-containing species may simply act as a catalyst for the oxidation of water by CrO_4^{2-} (thermodynamically unfavorable at 25°, but possibly favorable at 102°) but in that case would have to decompose slowly into species which were noncatalytic and nonoxidizable by CrO_4^{2-}. This N-containing species is not NO_2^- and its nature was not experimentally investigated further.

Decomposition by Explosion.—The explosive decomposition of solid $Cr(NH_3)_3(O_2)_2$ appears to require shock or sudden heating (see Experimental Section). This is in accord with our previous comments[4] that $Cr(NH_3)_3(O_2)_2$ is probably the most stable of the known diperoxoaminechromium(IV) compounds because of a high degree of hydrogen bonding in the crystal.

The explosive decomposition appears to go *ca.* 90% *via* the over-all reaction

$$Cr(NH_3)_3(O_2)_2(s) = {}^1/_2Cr_2O_3(s) + 3NH_3(g) + {}^5/_4O_2(g) \quad (4)$$

The apparent molecular weight of the gas produced was 22.5. The above equation would produce a gas of apparent molecular weight 21.4. The difference is probably within the experimental error but if taken at face value suggests the presence of one or more higher molecular weight constituents. Condensation of the NH_3 in a calibrated vacuum system indicated the gas contained *ca.* 85–90% of the NH_3 expected from the stoichiometry of eq 4. The infrared spectrum of the gas indicated the presence of *ca.* 5% N_2O (ν 2220 cm^{-1}) and *ca.* 1–2% H_2O in the background of a considerable quantity of NH_3 and O_2. No NO, NO_2, or O_3 was observed in the infrared spectrum. The mass spectrum of the gas gave mass peaks corresponding to NH_3, O_2, and H_2O, as well as a mass peak at 44 (N_2O) distinct from another at 44 (CO_2) noted in the background and a peak for N_2 (perhaps 1%). The N_2O mass peak was also observed when $Cr(NH_3)_3(O_2)_2$ was decomposed at *ca.* 150° on a hot filament directly in the mass spectrometer.[25] The mode of formation of N_2O is unknown.

Thus, in each mode of decomposition of $Cr(NH_3)_3(O_2)_2$ examined the decomposition products are not formed by a single stoichiometric reaction.

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[24] Control experiments with solutions 0.03 *F* in H_2O_2, 0.05 *F* in Na_2CrO_4, and 1 *F* in NaOH showed that 15–50% of any H_2O_2 formed would have remained after 2–3 min at 102°, whereas the 2-min value of Table II shows no loss of oxidation equivalents at that time.

[25] N_2O has also been observed as a product of nonexplosive thermal decomposition of $[Co(NH_3)_5]_2O_2^{5+}$ salts: R. G. Hughes and E. A. V. Ebsworth, unpublished observations.

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A Study of the Kinetics of Complex Formation between Hexacyanoferrate(III) Ions and Iron(III) to Form $FeFe(CN)_6$ (Prussian Brown)

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The kinetics of the reaction between iron(III) ion and hexacyanoferrate(III) ion to form the neutral complex $FeFe(CN)_6$ (Prussian Brown) have been investigated by the stopped-flow method. The complexation rate constant was determined over a $[H^+]$ range of 0.02–0.71 *M* at 25° and was found to increase with increase in basicity. Evidence of an autoreduction reaction to form $KFe^{III}Fe^{II}(CN)_6$ (Prussian Blue) and evidence of a very slow reaction (10–70 sec) were also observed.

Introduction

In an investigation by DeWet and Rolle[1] on the structure of $Fe^{III}Fe^{II}(CN)_6$, Prussian Green, and $Fe^{III}Fe^{III}(CN)_6 \cdot 2H_2O$, Prussian Brown, Prussian Green was found to contain mixed hexacyanoferrates with divalent iron predominating and the amount of divalent iron present depended on the method of preparation; how-

[1] J. F. DeWet and R. Rolle, *Z. Anorg. Allgem. Chem.*, **336**, 96 (1965).