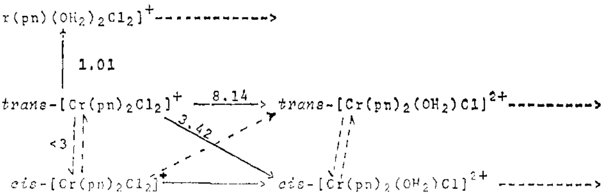

Figure 3.—First-order rate constants (10^5k, sec^{-1}) for aquation and isomerization reactions in 0.10 *F* HNO_3 at 35.0° in the absence of light.

rectly by three parallel first-order reactions. Alternative paths in which the *cis*-chloroaquo species is produced by isomerization of the *trans*-chloroaquo isomer or by isomerization of the *trans*-dichloro species followed by aquation cannot be ruled out. Garner and Esparza[8] did not observe cis → trans isomerization in the aquation of *cis*-$Cr(pn)_2Cl_2^+$. Spectrophotometric detection of trans → cis isomerization in the present study was precluded because of the reactivity of the primary products of aquation. It is also possible that cis isomerization products do not reach detectable concentrations since cis complexes generally aquate much faster than the trans. Mechanistic choices must await more complete characterization of the kinetics of aquation of the chloroaquo species of the bis(propylenediamine)chromium(III) system.

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Hydrolysis of Chromium(III)–Nitrito Complexes[1a]

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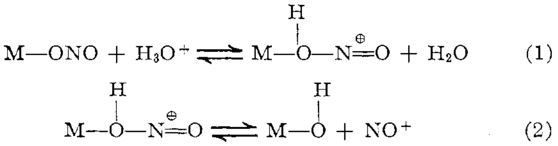
The acid- and nonacid-catalyzed hydrolysis reactions of *cis*- and *trans*-$Cr(en)_2(ONO)X^{n+}$ (en = ethylenediamine; X = ONO^-, OH_2, OH^-, F^-, Cl^-, Br^-, *N,N*-dimethylformamide (DMF), or dimethyl sulfoxide (DMSO)) have been examined. Rate and activation parameters have been evaluated for the first-order H^+-catalyzed and for some spontaneous ONO^--loss pathways. The acid-catalyzed reactions proceed with ~100% retention of geometrical configuration. Hydrolysis at pH 10.0–11.5 shows the following stereochemistries: *cis*-$Cr(en)_2(ONO)_2^+$ → 100% *cis*-$Cr(en)_2(ONO)OH^+$; *trans*-$Cr(en)_2(ONO)_2^+$ → 90–100% *trans*-$Cr(en)_2(ONO)OH^+$; *cis*-$Cr(en)_2(ONO)OH^+$ → 75% *cis*- + 25% *trans*-$Cr(en)_2(OH)_2^+$ (complicated by reactant isomerization); *trans*-$Cr(en)_2(ONO)OH^+$ → a pH-dependent distribution of 78% *trans*- (pH 10.0) to 95% *trans*-$Cr(en)_2(OH)_2^+$ (pH 11.5). Use of ^{18}O has revealed that hydrolysis of *cis*- and *trans*-$Cr(en)_2(ONO)_2^+$ in 0.1 *F* NaOH proceeds with Cr–O bond cleavage. Rate constants were also obtained for the cis ↔ trans isomerizations of $Cr(en)_2(ONO)OH^+$.

Introduction

By analogy with the behavior of cobalt(III)–carbonato complexes and the formation of the nitritopentaamminecobalt(III) ion in aqueous acidic solutions, Basolo and Pearson[2] predicted that acid hydrolysis of metal–nitrito (O-bonded nitrite) complexes should proceed *via* protonation, followed by "denitrosation" without the cleavage of the M–O bond, as represented by



$$M{-}ONO + H_3O^+ \rightleftharpoons M{-}\overset{\displaystyle H}{\overset{|}{O}}{-}\overset{\oplus}{N}{=}O + H_2O \qquad (1)$$

$$M{-}\overset{\displaystyle H}{\overset{|}{O}}{-}\overset{\oplus}{N}{=}O \rightleftharpoons M{-}\overset{\displaystyle H}{\overset{|}{O}} + NO^+ \qquad (2)$$

In a careful study of the acid hydrolysis of $Cr(NH_3)_5ONO^{2+}$, Matts and Moore[3] confirmed this prediction by finding a first-order dependence of the rate on $[H^+]$ at $[H^+] \leqslant 0.1\ M$. The rate enhancement in acid solution was so great when compared to the H^+ catalysis for species such as $Cr(OH_2)_5F^{2+}$,[4] which necessarily aquates with Cr–F bond fission, that CrO–N fission seemed more likely. However, side reactions involving ammonia loss prevented an accurate measurement of the uncatalyzed (spontaneous) hydrolysis rate and precluded a direct determination of bond-cleavage position in the acid-catalyzed reaction.

While the tendency toward amine loss is not entirely eliminated in $Cr(en)_2XY^{n+}$ hydrolysis,[5] it is vastly di-

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(2) F. Basolo and R. G. Pearson, "Mechanisms of Inorganic Reactions," 2nd ed, Wiley, New York, N. Y., 1967, p 229.

(3) T. C. Matts and P. Moore, *J. Chem. Soc. A*, 219 (1969). In view of the investigations of these authors, several earlier studies of $Cr(NH_3)_5ONO^{2+}$ hydrolysis may be of dubious significance; see, *e.g.*, V. Holba, *Chem. Zvesti*, **22**, 81 (1968); D. Banerjea and C. Chatterjee, *Z. Anorg. Allg. Chem.*, **361**, 99 (1968); A. Liberti and L. Ciavatta, *J. Inorg. Nucl. Chem.*, **8**, 365 (1958).

(4) T. W. Swaddle and E. L. King, *Inorg. Chem.*, **3**, 234 (1964); **4**, 532 (1965).

(5) See, *e.g.*, (a) D. J. MacDonald and C. S. Garner, *J. Amer. Chem. Soc.*, **83**, 4152 (1961); (b) D. J. MacDonald and C. S. Garner, *Inorg. Chem.*, **1**, 20 (1962); (c) J. M. Veigel and C. S. Garner, *ibid.*, **4**, 1569 (1965); (d) C. Y. Hsu and C. S. Garner, *Inorg. Chim. Acta*, **1**, 17 (1967); (e) J. M. Veigel, *Inorg. Chem.*, **7**, 69 (1968); (f) S. H. Caldwell and D. A. House, *J. Inorg. Nucl. Chem.*, **31**, 811 (1969).

minished. Further, information on the steric course of X and Y loss can be obtained.[6] Also the effect of, *e.g.*, varied X on the rate of loss of a constant Y may provide data of value in assessing the possible mechanisms of reaction. Thus the species $Cr(en)_2(ONO)X^{n+}$ is a more sensitive and versatile probe than $Cr(NH_3)_5ONO^{2+}$ for the kinetic characterization of the Cr–ONO moiety. The present work is concerned with the hydrolysis behavior of a number of $Cr(en)_2(ONO)X^{n+}$ complexes in aqueous solution in the pH range 0.8–11.5.

Experimental Section

Preparation of Complexes.—Preparation, characterization, and analysis of most of the solid complexes have been reported elsewhere.[7,8] The *trans*-$[Cr(en)_2(ONO)F]ClO_4$ was prepared by a published method[9] and analyzed satisfactorily.

Although most kinetic work on *trans*-$Cr(en)_2(ONO)OH_2^{2+}$ and *trans*-$Cr(en)_2(ONO)OH^+$ utilized solid salts as their source,[8] *trans*-$Cr(en)_2(ONO)OH_2^{2+}$ was initially isolated by cation-exchange separation from *trans*-$Cr(en)_2(ONO)_2^+$ hydrolysis mixtures (addition of base then being used when the hydroxo complex was desired). The ion-exchange procedure, also extensively applied in kinetic studies, was as follows.

About 36 mg (*ca.* 0.1 mmol) of *trans*-$[Cr(en)_2(ONO)_2]ClO_4$ was dissolved in 20 ml of 0.01 F $HClO_4$ and kept at 25° for 10 min. The solution was charged onto a 5-cm × 1-cm² column of Na^+ Dowex AG50W-X8 resin (100–200 mesh) jacketed at 0°. After the resin was washed with 30 ml of H_2O, elution with 50 ml of pH 3 0.5 F $NaClO_4$ over 10 min removed unreacted *trans*-$Cr(en)_2(ONO)_2^+$ and elution with 50 ml of pH 3 1.5 F $NaClO_4$ then produced an effluent *ca.* 0.04 mM in a complex with an NO_2^-:Cr mole ratio of 1.01 ± 0.01. The electronic spectrum of this eluate was identical with those of later solid preparations of the double salt *trans*-$[Cr(en)_2(ONO)OH_2](ClO_4)_2 \cdot$ *trans*-$[Cr(en)_2(ONO)OH]ClO_4 \cdot H_2O$ dissolved in acidic solutions.[8] Reaction between equimolar *trans*-$Cr(en)_2(ONO)Br^+$ and $Hg(ClO_4)_2$[8] in 0.005 F $HClO_4$ also produces a solution of pure *trans*-$Cr(en)_2(ONO)OH_2^{2+}$ within 30 sec at 20°.

If one substitutes *cis*-$[Cr(en)_2(ONO)_2]ClO_4$ for the trans isomer and 0.001 F for 0.01 F $HClO_4$, the above procedure can be used to provide an essentially quantitative yield of *cis*-$Cr(en)_2(ONO)OH_2^{2+}$; the NO_2^-:Cr mole ratio of the 1.5 F $NaClO_4$ eluate was 1.00 ± 0.02. This complex can be more conveniently prepared from *cis*-$[Cr(en)_2(ONO)Cl]ClO_4$ by dissolution in 0.001 F $HClO_4$; within 30 sec the complex stereoretentively undergoes complete Cl^- loss, so that cation-exchange separation is unnecessary. In basic medium a pure solution of *cis*-$Cr(en)_2(ONO)OH^+$ is produced within the same period.

Preparation of Media.—Studies of *cis*-$Cr(en)_2F_2^+$[10] have shown acid-catalyzed metal complex hydrolysis to be possibly sensitive to the nature of the reaction medium. Thus, in the acid-to-neutral pH region the use of buffer systems was deliberately avoided in the present work; at high pH, ethylenediamine buffers were used in an attempt to repress any amine-loss side reactions.[11] An ionic strength of 0.150 ± 0.005 M (controlled with $NaClO_4$) was used throughout.

Perchloric acid was prepared by dilution of the AR 72% acid and standardized against HgO. Standard $NaClO_4$ was prepared from AR Na_2CO_3 neutralized with AR $HClO_4$. Ethylenediamine buffers were prepared from standard $HClO_4$ and $NaClO_4$ and 98% en, dried and distilled over KOH. All other chemicals were reagent grade.

Rate Measurements.—The sensitivity of $Cr(en)_2(ONO)X^{n+}$ complexes to acid necessitated the use of several techniques of rate measurement.

At initial complex concentrations below 0.002 M, pH changes resulting from release of the weak base NO_2^- were negligible provided the reaction was followed only to 50–75% completion when $[H^+] \geqslant 0.01$ M and to *ca.* 90% completion when $[H^+] \leqslant 0.15$ M. Thus, over the range $0.15 \geqslant [H^+] \geqslant 0.01$ M, following the reaction by constant-wavelength spectrophotometric scanning (in the range 310–330 nm) could be used. Reaction was begun by mixing in ⩽5 sec 5 ml each of prethermostated complex and $HClO_4$–$NaClO_4$ solution in the 4-cm thermostated cell of a Shimadzu SV50A spectrophotometer; zero time was taken at half-mixture. At 10–20° reactions were slow enough at some acidities to allow isosbestic points to be located by repetitive scanning of the wavelength region from 320 to 650 nm. For the rather labile and sparingly soluble *cis*-$[Cr(en)_2(ONO)_2]ClO_4$ the procedure was modified by making up a concentrated solution of the complex in the inert solvent DMF and rapidly mixing 0.1 ml of this into 10 ml of thermostated acid medium. We have assumed that the 1% DMF solution resulting from this modified procedure is not significantly different from the usual aqueous solution with regard to the reaction rates involved here.

In media of pH >2 pH control became necessary. Reactions in such media were sufficiently slow to permit manual adjustment with 1 F NaOH or $HClO_4$ added from a micropipet. Nonetheless, measurements at short pH intervals were not possible. Changes in pH were further minimized by use of the lowest possible complex concentrations.

Because of the complexity of its hydrolysis in the neutral pH region, *trans*-$Cr(en)_2(ONO)_2^+$ was examined by cation-exchange chromatography as well as by spectrophotometry in an attempt to identify the reaction products. To prevent acid-catalyzed decomposition of ONO^-, the resin was not used in the H^+ form. Rather, the Dowex AG50W-X8 resin was used in the Na^+ form and elutions were made at 0° with $NaClO_4$ (or occasionally NaCl or $NaNO_3$) solutions. The *trans*-$Cr(en)_2(ONO)_2^+$ could be readily eluted by 0.4–0.5 F $NaClO_4$ and thus separated from *trans*-$Cr(en)_2(ONO)OH_2^{2+}$ (which required 1.5 F $NaClO_4$) provided eluates were adjusted to pH 3 to prevent proton loss from the aquo ligand. However, *cis*-$Cr(en)_2(ONO)OH_2^{2+}$ was found to coeluate with the trans isomer, and *cis*-$Cr(en)_2(ONO)_2^+$ aquates too rapidly to survive the chromatography. Retention of *trans*-$Cr(en)_2(ONO)_2^+$ by the resin is ⩽90% at concentrations ⩽0.1 mM, and *cis*- and *trans*-$Cr(en)_2(OH_2)OH^{2+}$ and their reaction products are partially eluted by pH 3 1.5 F $NaClO_4$. Owing to these factors, the only useful studies of *trans*-$Cr(en)_2(ONO)_2^+$ made by cation exchange were at 2–4 mM in pH 6 0.15 F $NaClO_4$, and these provided accurate data only on ONO^- release and *trans*-$Cr(en)_2(ONO)_2^+$ disappearance rates.

It was found that Cl^- Dowex AG1-X8 anion-exchange resin retains NO_2^- completely down to at least 5 μM. Hence, measurement of NO_2^- release rates for all the complexes at *ca.* 0.2 mM in media at pH >2 could readily be determined by anion-exchange methods. Typically, 5-ml aliquots were withdrawn at chosen intervals and adsorbed on a 5-cm × 1-cm² column of resin jacketed at 0°.[12] The column was washed with 30 ml of H_2O and then eluted with 100 ml of 1 F NaCl, the initial effluent plus water wash and NaCl eluates being collected separately in 100-ml flasks. The solutions were warmed to 20°, made up to 100.0 ml, and analyzed for NO_2^-. The total NO_2^- (NaCl eluate) was used to estimate any loss of NO_2^- (*via* HONO decomposition) from the reaction medium. Generally, this was negligible,

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[6] In the main, the simple aquation reactions of $Cr(en)_2XY^{n+}$ species appear to be highly stereoretentive; see, *e.g.*, C. S. Garner and L. P. Quinn, *Inorg. Chem.*, **3**, 1348 (1964); C. S. Garner and D. A. House, *Transition Metal Chem.*, **6**, 200 (1970).

[7] W. W. Fee, C. S. Garner, and J. N. MacB. Harrowfield, *Inorg. Chem.*, **6**, 87 (1967).

[8] W. W. Fee, J. N. MacB. Harrowfield, and W. G. Jackson, *J. Chem. Soc. A*, in press.

[9] J. W. Vaughn, O. J. Stvan, Jr., and V. E. Magnuson, *Inorg. Chem.*, **7**, 736 (1968).

[10] K. R. A. Fehrmann and C. S. Garner, *J. Amer. Chem. Soc.*, **83**, 1276 (1961).

[11] (a) F. Woldbye, *Acta Chem. Scand.*, **12**, 1079 (1958); (b) D. C. Olson and C. S. Garner, *Inorg. Chem.*, **2**, 415 (1963).

[12] Before adsorption, aliquots were diluted with 20 ml of H_2O to prevent ClO_4^- elution of NO_2^-, and where necessary, sufficient 0.1 F NaOAc was added to change the pH to ⩾6 and prevent HONO from passing through the column.

but, where appreciable, only the complexed nitrite (effluent plus H_2O wash) analyses were used to estimate ligand ONO^- release.

While the complicated and ill-characterized reactions of the labile $Cr(en)_2(OH)OH_2^{2+}$ isomers virtually precluded accurate spectrophotometric rate measurements at $2 \lesssim pH \leqslant 10$ (control of pH and HONO reactions required this range), it was expected from the fact that $Cr(en)_2(OH)_2^+$ species may be equilibrated in en buffers[11a] that slow reactions at high pH could be studied in en buffers by repetitive spectrophotometric scans, thus providing evidence of base hydrolysis paths. Accordingly, two buffers were prepared, one 0.075 *M* in en, 0.075 *F* in $enHClO_4$, and 0.075 *F* in $NaClO_4$ (pH 10.0) and the other 0.15 *M* in en and 0.15 *F* in $NaClO_4$ (pH 11.5). Reactions were then examined by spectral scanning on a Beckman DK2A instrument with thermostated cell block.

Chemical Analyses.—Chromium was determined spectrophotometrically after conversion to CrO_4^{2-}.[7] Some NO_2^- analyses were made by the method of Rao and Pandalai,[13] but a generally superior method, especially suited to the low concentrations (*ca.* $\leqslant 4.5.10^{-5}$ *F*) encountered in eluates of anion-exchange experiments, was developed. The following method based on the colorimetric azo dye type analysis reported by Vogel was used.[14]

Three solutions, A, B, and C, were prepared. Solution A contained 1.2 g of sulfanilic acid and 40 ml of 12 *F* HCl made up to 1 l. with distilled water, B had 1.0 g of naphthylamine and 4 ml of 12 *F* HCl made up to 1 l., and C was 0.4 *F* NaOAc. An aliquot of NO_2^- solution containing not more than 0.45 μmol of NO_2^- was mixed with 10 ml of A and allowed to react for 5 min; 10 ml of B and 10 ml of C were then added, and 15 min was allowed for complete azo dye formation. After making up to a final volume of 100 ml with distilled water the absorbance *A* of this solution at 520 nm was measured for a 4-cm path. Under these conditions a linear Beer's law plot was obtained; some curvature was apparent with greater quantities of NO_2^-.

Kinetic Analysis.—In systems other than *cis*- and *trans*-$Cr(en)_2(ONO)_2^+$ first-order rate plots of log $(A - A_\infty)$ or log $(100 - \%NO_2^-$ released) *vs.* time could be applied. For *cis*-$Cr(en)_2(ONO)_2^+$ the method used by Ashley and Hamm[15] for $Cr(DMSO)_2(ox)_2^-$ was convenient. The "time-ratio" modification[16] of the method of Swain[17] for consecutive first-order reactions was used for *trans*-$Cr(en)_2(ONO)_2^+$; the time-ratio plots necessarily involved the region of shallow minima, leading to double solutions for the successive rate constants k_1 and k_2 and requiring an independent study of *trans*-$Cr(en)_2(ONO)OH_2^{2+}$ to obtain k_2.

^{18}O Measurements.—Measurements of ^{18}O content were made on aquo complexes formed in acidic ^{18}O-enriched water and on ONO^- released in ^{18}O-enriched 0.1 *F* NaOH. Enriched water (1.67% ^{18}O) was purchased from Yeda Research and Development Co., Rehovoth, Israel. Concentrated HCl in $H_2{}^{18}O$ was prepared by bubbling dry HCl gas into the ice-cooled water until saturated. Enriched 0.1 *F* NaOH in $H_2{}^{18}O$ was prepared by dissolving AR NaOH in $H_2{}^{18}O$. Aquo complexes were precipitated as anhydrous chlorides by addition of concentrated HCl and acetone to their solution formed from nitrito complex and acids;[8] ligand H_2O was converted to CO_2 with guanidine hydrochloride,[18] using the method of Moore, Basolo, and Pearson.[19] Nitrite released in base was converted to N_2O by reaction with buffered azide.[20] Mass spectral measurements on CO_2 and N_2O were made on an AEI MS9 instrument.

Results

Since *trans*-$Cr(en)_2(ONO)_2^+$ was studied in greatest detail, its behavior forms a convenient basis for description of the other systems.

Reaction Course.—Use of several $Cr(en)_2(ONO)X^{n+}$ complexes in preparative work[8] has shown that in concentrated acid a facile and predominantly stereoretentive replacement of ligand ONO by OH_2 occurs. The spectral changes observed when *trans*-$Cr(en)_2(ONO)_2^+$ and *trans*-$Cr(en)_2(ONO)OH_2^{2+}$ react in relatively dilute acid are shown in Figure 1. The coincidence of isosbestic points obtained is perhaps not surprising in view of the similar ligand fields of OH_2 and ONO^- [21] and the fact that absorption due to metal ion chromophore in the 300–400-nm region is only a minor contribution. Under no conditions was spectral evidence for protonation of $Cr(en)_2(ONO)X^{n+}$ obtained, the isosbestic points of Figure 1 being in excellent agreement with those calculated for the appropriate combinations of *trans*-$Cr(en)_2(ONO)_2^+$, *trans*-$Cr(en)_2(ONO)OH_2^{2+}$, *trans*-$Cr(en)_2(OH_2)_2^{3+}$, and HONO spectra. The point at 521 ± 1 nm is most precisely definitive of steric course, and its uncertainty of definition would allow at most 4% overall formation of *cis*-$Cr(en)_2(OH_2)_2^{3+}$. Even higher retention of configuration was suggested by experiments in which *trans*-$Cr(en)_2(ONO)_2^+$ was treated with 1 *F* $HClO_4$ containing N_3^- or urea (to destroy HONO) and the 320–600-nm product spectrum was compared with that of *trans*-$Cr(en)_2(OH_2)_2^{3+}$; virtual

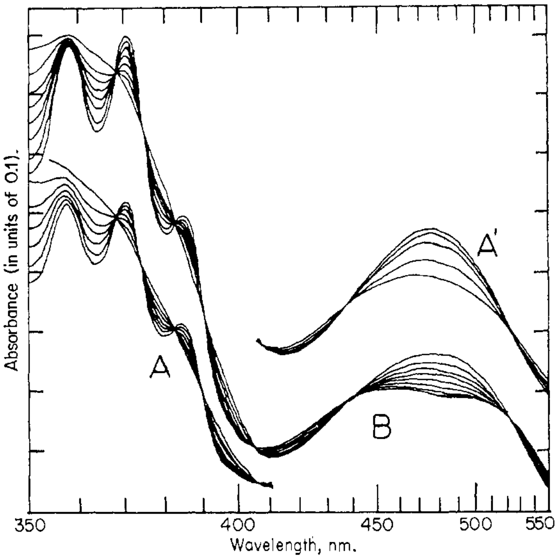

Figure 1.—Spectral changes in primary and secondary hydrolysis of *trans*-$Cr(en)_2(ONO)_2^+$ in 0.075 *M* H^+: A and A′, *trans*-$Cr(en)_2(ONO)_2^+$ (two different concentrations) at 17°; reading down at 350 nm, reaction time is 0.5, 3.5, 6.5, 9.5, 13.0, 18.0, and 25.0 min for A, and reading down at 470 nm, reaction time is 0.7, 1.5, 3.5, 6.7, and 10.7 min for A′; B, *trans*-$Cr(en)_2(ONO)OH_2^{2+}$ at 2°; reading down at 470 nm, reaction time is 0.25, 4.0, 8.0, 13.0, 20.0, 32.0, 53.0, and 83.0 min; the ordinate scales for scans A and A′ are arbitrarily displaced to facilitate display.

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(13) G. G. Rao and K. M. Pandalai, *Analyst*, **59**, 99 (1934).

(14) A. I. Vogel, "Textbook of Quantitative Inorganic Analysis," Longmans, Green and Co., London, 1961, p 784.

(15) K. R. Ashley and R. E. Hamm, *Inorg. Chem.*, **5**, 1645 (1966).

(16) A. A. Frost and R. G. Pearson, "Kinetics and Mechanism," 2d ed, Wiley, New York, N. Y., 1961, p 170.

(17) C. G. Swain, *J. Amer. Chem. Soc.*, **66**, 1696 (1944).

(18) P. D. Boyer, D. V. Graves, C. H. Suelter, and M. E. Dempsey, *Anal. Chem.*, **33**, 1906 (1961).

(19) P. Moore, F. Basolo, and R. G. Pearson, *Inorg. Chem.*, **5**, 223 (1966).

(20) M. Anbar and H. Taube, *J. Amer. Chem. Soc.*, **76**, 6243 (1954).

(21) W. W. Fee and J. N. MacB. Harrowfield, *Aust. J. Chem.*, **23**, 1049 (1970).

identity was observed and no systematic differences consistent with the presence of *cis*-$Cr(en)_2(OH_2)_2{}^{3+}$ were apparent. Complete stereoretentivity of nitrite loss in acid was indicated by application of both of these types of measurement to *cis*-$Cr(en)_2(ONO)_2{}^{+}$ and *cis*-$Cr(en)_2(ONO)OH_2{}^{2+}$ also. Spectral changes observed with these species are shown in Figure 2. Comparison of Figures 1 and 2 suggests that the common isosbestic points between 350 and 400 nm arise as a characteristic of the Cr–ONO and Cr–OH_2 chromophores in the presence of HONO, and this is supported by the data of Table I.

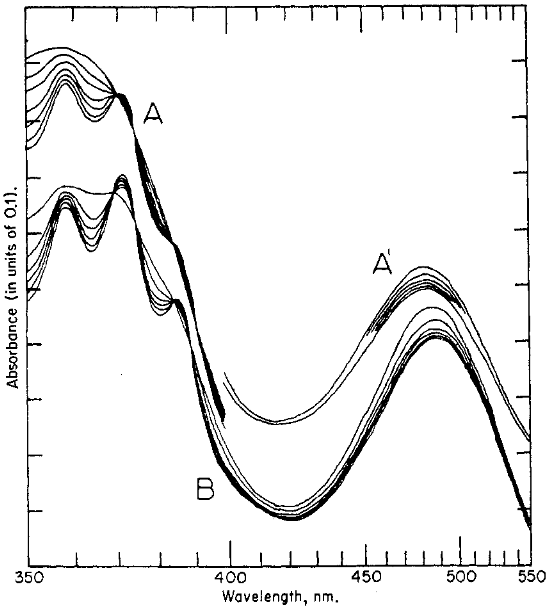

Figure 2.—Spectral changes in primary and secondary hydrolysis of *cis*-$Cr(en)_2(ONO)_2{}^{+}$ in acidic solution: A and A′, *cis*-$Cr(en)_2(ONO)_2{}^{+}$ (two different concentrations) in 0.005 *M* H^+ at 12°; reading down at 350 nm, reaction time is 0.5, 1.5, 3.2, 6.0, 9.1, 13.1, and 19.0 min for A, and reading down at 480 nm, reaction time is 0.5, 2.2, 4.2, 6.0, 7.8, and 11.3 min for A′; B, *cis*-$Cr(en)_2(ONO)OH_2{}^{2+}$ in 0.075 *M* H^+ at 17°; reading down at 350 nm, reaction time is 0.4, 3.4, 6.3, 9.5, 15, and 25 min; the ordinate scales for scans A and A′ are arbitrarily displaced to facilitate display.

TABLE I

OBSERVED ISOSBESTIC POINTS IN *trans*-$Cr(en)_2(ONO)X^{n+}$ ACID-CATALYZED HYDROLYSIS AND CALCULATED POINTS FOR THE REACTION

$$trans\text{-}Cr(en)_2(ONO)X^{n+} \longrightarrow 100\%\ trans\text{-}Cr(en)_2(OH_2)X^{(n+1)+}$$

X		λ, nm
ONO^-	Obsd[a]	368, 373, 383, 390, 406, 438, 521
	Calcd[b]	436, 521
F^-	Obsd[a]	366, 373, 381, 392, 402, 444, 528
	Calcd[b]	444, 528
Cl^-	Obsd[a]	368, 373, 382, 389, 402, 454, 562
	Calcd[b]	454, 562
Br^-	Obsd[a]	369, 373, 382, 389, 402, 454, 572
	Calcd[b]	448, 572
DMF	Obsd[a]	369, 374, 384, 389, 408, 440, 520
	Calcd[b]	442, 520

[a] Uncertainty ±1 nm. [b] Calculated isosbestic points for $\lambda < 400$ nm are not included since these do not define steric course.

When spectral changes were observed for *trans*-$Cr(en)_2(ONO)_2{}^{+}$ reacting in solutions of pH 2–8, well-defined isosbestic points were not obtained. Though at low pH HONO decomposition partly accounts for this, the major effect appears to be from product reactions representing the increasing involvement of the labile[11a] $Cr(en)_2(OH_2)OH^{2+}$ species. Thus, while the initial spectral changes suggested no radical divergence from the simple stereoretentive reaction scheme found at pH <2, accurate definition was impossible without knowledge of the kinetic behavior of *trans*-$Cr(en)_2(OH_2)OH^{2+}$. Independent study showed this to be complex, involving at least isomerization, en loss, and polymerization, and these factors were not quantitatively elucidated. Hence, spectrophotometry gave no accurate information on the course of *trans*-$Cr(en)_2(ONO)_2{}^{+}$ hydrolysis in the pH region where *trans*-$Cr(en)_2(OH_2)OH^{2+}$ could be a significant product.

Under conditions where *trans*-$Cr(en)_2(ONO)_2{}^{+}$ hydrolysis was slow enough to be followed *via* cation-exchange chromatography, any mononitrito hydrolysis intermediate was found to be present in such small concentrations as to prohibit its characterization thereby precluding establishment of the steric course of even the first ONO^- loss from *trans*-$Cr(en)_2(ONO)_2{}^{+}$. From their spectra, 0.5 *F* $NaClO_4$ eluates were shown to contain only *trans*-$Cr(en)_2(ONO)_2{}^{+}$, and it is apparent that this was the only nitrito complex present in significant concentrations at any reaction time. The $NO_2{}^{-}$:Cr ratios measured for 1.5 *F* $NaClO_4$ eluates showed that Cr(III) species other than nitrito complexes were always present in at least comparable concentrations. Independent anion-exchange kinetic runs with *trans*-$Cr(en)_2(ONO)OH_2{}^{2+}$–$Cr(en)_2(ONO)OH^{+}$ gave rate constants consistent with stereoretentive consecutive nitrito loss from *trans*-$Cr(en)_2(ONO)_2{}^{+}$.

In en buffers it is possible to establish equilibrium between the slowly reacting *cis*- and *trans*-$Cr(en)_2(OH)_2{}^{+}$ complexes,[11] thus allowing a study of the *trans*-$Cr(en)_2(ONO)_2{}^{+}$ hydrolysis in high-pH en buffers where problems arising from final product reactions might be overcome. On the other hand, the likelihood of involvement of labile $Cr(en)_2(ONO)OH^{+}$ species and the possible similarity of *trans*-$Cr(en)_2(ONO)_2{}^{+}$ hydrolysis and $Cr(en)_2(OH)_2{}^{+}$ isomerization rates could provide a system very complex to analyze. However, initial spectral changes for *trans*-$Cr(en)_2(ONO)_2{}^{+}$ in en buffer showed isosbestic points at 435 and 495 nm, closely consistent with those expected for reaction 3. Though

$$trans\text{-}Cr(en)_2(ONO)_2{}^{+} + OH^{-} \longrightarrow 100\%\ trans\text{-}Cr(en)_2(ONO)OH^{+} + ONO^{-} \quad (3)$$

sharp isosbestic points were not maintained, the drift from those expected for complete retention in the primary ONO^- loss was not rapid and the extent of formation of *cis*-$Cr(en)_2(ONO)OH^{+}$ is therefore estimated to be not greater than 10%.

The rapid primary hydrolysis of *cis*-$Cr(en)_2(ONO)_2{}^{+}$ in en buffers was examined only by means of constant-wavelength absorbance measurements. However, kinetic analysis (see below) showed that the reaction path involved made an appreciable contribution in 0.01 *F* $HClO_4$ also, and spectral scanning in that medium established stereoretentivity for all conditions. The en buffer reactions of both *cis*- and *trans*-$Cr(en)_2(ONO)OH^+$ were slow enough to be studied by repetitive scanning. These results proved complicated. With *trans*-$Cr(en)_2(ONO)OH^+$ a single reasonably sharp isosbestic point was obtained in both buffers, a slight drift being consistent with the known isomerization reactions of the expected *cis*- and *trans*-$Cr(en)_2(OH)_2^+$ products. However, the isosbestic point at pH 11.5 was not the same as at pH 10.0 and indicated a decrease from 95% *trans*-$Cr(en)_2(OH)_2^+$ product at pH 11.5 to 78% at pH 10.0. In contrast, *cis*-$Cr(en)_2(ONO)OH^+$ gave essentially the same spectral behavior in these two buffers, without sharply defined isosbestic points. The estimated initial isosbestic point corresponded to formation of 75% *cis*- and 25% *trans*-$Cr(en)_2(OH)_2^+$, this amount of cis being less than that present at equilibrium in the $Cr(en)_2(OH)_2^+$ system,[11b] so that the isosbestic-point drift was in a direction inconsistent with product isomerization (as well as being too fast to be explained thus). This drift was in fact indicative of reactant isomerization, so that the reaction scheme was at least as complicated as

$$\begin{array}{ll} cis\text{-Cr(en)}_2\text{(ONO)OH}^+ + \text{OH}^- \xrightarrow{k_H} & \\ k_i \downarrow\uparrow & cis\text{- and } trans\text{-Cr(en)}_2\text{(OH)}_2^+ + \text{NO}_2^- \quad (4) \\ trans\text{-Cr(en)}_2\text{(ONO)OH}^+ & \end{array}$$

The only other $Cr(en)_2(ONO)X^{n+}$ system examined at high pH was that of *trans*-$Cr(en)_2(ONO)F^+$. Although sharp isosbestic points were observed and ONO^- loss appeared to be the reaction occurring, the substitution was not stereoretentive, and since *cis*-$Cr(en)_2(OH)F^+$ has not been characterized, this system could not be fully interpreted.

Rates.—Some representative hydrolysis rate data for *trans*-$Cr(en)_2(ONO)_2^+$ are illustrated in Figure 3. The full curves shown are those calculated from the experimental first-order rate constant, k_e, using the expression $k_e = k_0 + k_H[H^+]$. The values of k_0 and k_H used are given in Table II. The only points which show some suggestion of a systematic deviation from this rate law are those for en buffers of pH 10.0 and 11.5. Since rates in both en buffers were identical at any one temperature, it is probable that these deviations represent a medium effect due to the change from Na^+ to H^+ in varying pH at constant ionic strength, rather than any OH^--dependent reaction. The important feature of these curves is the sharp rise in rate at low pH. For $[H^+] \geqslant 0.01$ *M* this dependence is such that the relation $k_e = k_H[H^+]$ is fitted within experimental error. The generality of this relationship was demonstrated by the study of other *trans*-$Cr(en)_2(ONO)X^{n+}$ complexes, and a sample of these results is given in Figure 4 (X = F^-, Cl^-, DMF).

TABLE II

SPONTANEOUS AND ACID-CATALYZED RATE CONSTANTS FOR HYDROLYSIS OF *trans*-$Cr(en)_2(ONO)_2^+$ OVER pH RANGE 1–11.5 ($I = 0.15$ *M*)

Temp, °C	10^5k_0,[a] sec^{-1}	10^2k_H,[a] M^{-1} sec^{-1}
25.3	1.6	7.2
30.0	3.2	13.2
34.0	5.1	24.6

[a] Values used in $k_e = k_0 + k_H[H^+]$ to obtain full curves of Figure 3.

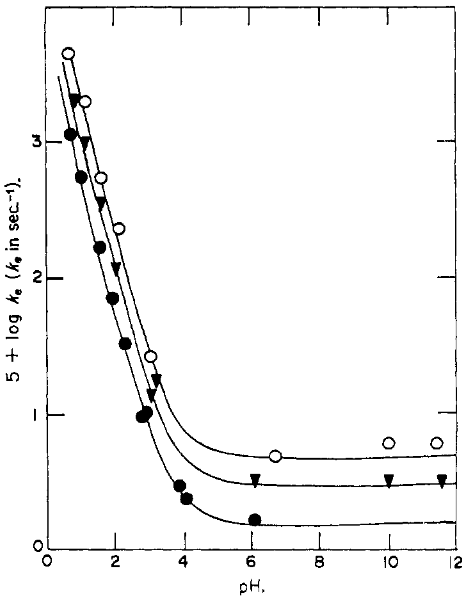

Figure 3.—Dependence of rate of primary hydrolysis of *trans*-$Cr(en)_2(ONO)_2^+$ on pH ($I = 0.15$ *M*): ○, 34.0°; ▼, 30.0°; ●, 25.3°.

The *cis*- and *trans*-$Cr(en)_2(ONO)OH_2^{2+}$ hydrolyses also showed such a H^+ dependence. For *cis*-$Cr(en)_2$-

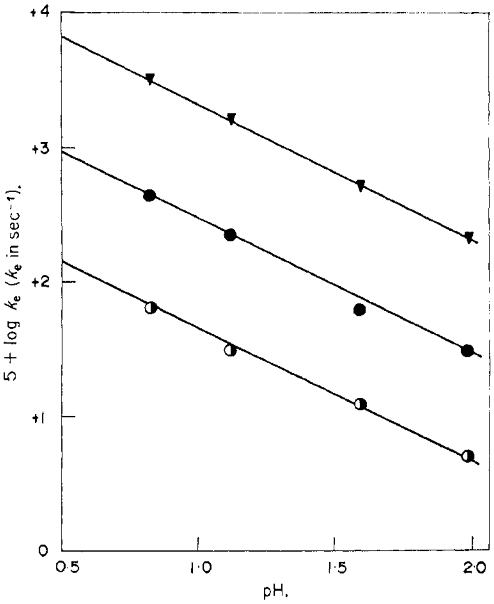

Figure 4.—Representative rate data for acid-catalyzed hydrolysis of *trans*-$Cr(en)_2(ONO)X^{n+}$ ($I = 0.15$ *M*): ◑, X = F^-, 15.8 ± 0.1°; ●, X = Cl^-, 25.2 ± 0.1°; ▼, X = DMF, 33.9 ± 0.1°; slope of full lines is 1.0.

$(ONO)_2^+$ the k_0 term contributes appreciably to k_e even in 0.01 *M* H^+, and k_H was taken as $(k_e - k_0)/[H^+]$ (rather than simply as $k_e/[H^+]$ as for the other complexes).

Table III gives the activation parameters for the acid-catalyzed hydrolysis of *cis*- and *trans*-$Cr(en)_2(ONO)X^{n+}$ at 25°, together with data on $Cr(NH_3)_5ONO^{2+}$ and $Cr(OH_2)_5ONO^{2+}$ for comparison purposes.

TABLE III

KINETIC PARAMETERS FOR THE ACID-CATALYZED ONO^- LOSS FROM *cis*- AND *trans*-$Cr(en)_2(ONO)X^{n+}$ (I = 0.15 *M*), $Cr(NH_3)_5ONO^{2+}$ (I = 1 *M*), AND $Cr(OH_2)_5ONO^{2+}$ (I = 1.0 *M*) AT 25°

Complex	10^2k_H,[a] M^{-1} sec^{-1}	$\Delta H^{\ddagger}$,[b] kcal mol^{-1}	$\Delta S^{\ddagger}$,[b] cal deg^{-1} mol^{-1}
trans-$Cr(en)_2(ONO)_2^+$	6.5	24.3 ± 0.7	+17.6 ± 2.4
trans-$Cr(en)_2(ONO)OH_2^{2+}$	9.6	19.8 ± 0.8	+3.2 ± 2.6
cis-$Cr(en)_2(ONO)_2^+$	50	22 ± 2.0[c]	+18 ± 7[d]
cis-$Cr(en)_2(ONO)OH_2^{2+}$	13	20.1 ± 0.3	+4.9 ± 0.9
trans-$Cr(en)_2(ONO)Cl^+$	2.8	21.0 ± 0.5	+4.9 ± 1.6
trans-$Cr(en)_2(ONO)Br^+$	3.6	20.3 ± 0.8[c]	+3 ± 3[d]
trans-$Cr(en)_2(ONO)DMF^{2+}$	7.6	20.1 ± 0.5	+3.8 ± 1.5
trans-$Cr(en)_2(ONO)DMSO^{2+}$	8.0	...	...
cis-$Cr(en)_2(ONO)F^+$	1.6	20.9 ± 0.4	+3.4 ± 1.3
$Cr(NH_3)_5ONO^{2+}$	30[d]	19.7 ± 0.8[d]	+5 ± 3[d]
$Cr(OH_2)_5ONO^{2+}$	198[e]	19.8 ± 0.7[e]	+9 ± 2[e]

[a] Except as noted, all results are from this research. [b] Except as noted, the activation parameters were obtained by fitting k_H values to the absolute reaction rate theory equation by nonlinear least-squares means using the Fortran Library Program G2-002 on the IBM 7044 computer at Melbourne; this equation described all k_H values within experimental error over the range 10–40°; the errors are standard errors. [c] Manual fitting of k_H values (only a few runs were made on these complexes); errors are mean deviations from the mean. [d] Reference 3. [e] T. C. Matts and P. Moore, *J. Chem. Soc. A*, 1997 (1969).

The complete pH dependencies of the hydrolysis of *cis*- and *trans*-$Cr(en)_2(ONO)OH_2^{2+}$ were complicated by proton loss from the aquo ligand, and this effect, coupled with the inability to maintain precise pH control over the "end point" regions, rendered estimation of k_0 values for these cations exceedingly approximate. Figure 5 illustrates some results for *cis*- and *trans*-$Cr(en)_2(ONO)OH_2^{2+}$ (in equilibrium with proportions of the hydroxo complex dependent on the pH) at 25.3° at which temperature independent spectrophotometric measurements of the acid dissociation constant K_a gave K_a = 4.8 (trans) and 5.7 (cis). The full curves are calculated for

$$k_e = \frac{k_{01} - k_H[H^+] + (k_{02}K_a/[H^+])}{1 + (K_a/[H^+])} \qquad (5)$$

which results from a general-acid catalysis treatment for $Cr(en)_2(ONO)OH_2^{2+}$ species, assuming an hydrolysis rate of the form $k_e = k_{01} + k_H[H^+]$ for the aquo complex and $k_e = k_{02}$ for the hydroxo complex (*i.e.*, negligible pH dependence is assumed for hydrolysis of the hydroxo complex over the pH range where it is present in appreciable amounts). From trial-and-error fitting to eq 5 upper limits to k_{01} values could be determined. However, it will be noted in Figure 5 that each calculated curve is a poor fit to the experimental points at high pH. This derives essentially from the use of pH ~7 anion-exchange ONO^--release measurements of k_e as k_{02}, and since k_e(calcd) is then an overestimate at higher pH, this was taken as circumstantial evidence for the suppression in en buffers of reaction paths involving en loss (which presumably would produce very labile polyhydroxo species). Though it is possible that the change in reaction medium could explain these results, an effect opposite to and of far greater magnitude than that on *trans*-$Cr(en)_2(ONO)_2^+$ (see above) would have to be postulated. However, it should be noted that the behavior of both *cis*- and *trans*-$Cr(en)_2(ONO)OH^+$ in en buffers is not simple, and the present work on them constitutes only a relatively superficial investigation. Spectral changes for *cis*-$Cr(en)_2(ONO)OH^+$ were analyzed in accord with eq 4, involving both hydrolysis and isomerization. Rate plots were constructed for 333 nm (an isosbestic point for *cis*- and *trans*-$Cr(en)_2(OH)_2^+$ and close to one for *cis*- and *trans*-$Cr(en)_2(ONO)OH^+$) and 485 nm (an isosbestic point for *trans*-$Cr(en)_2(ONO)OH^+$ and the 75% *cis*- and 25% *trans*-$Cr(en)_2(OH)_2^+$ product indicated by the "initial isosbestic point" for the system), and the hydrolysis rate constant k_H and the cis-to-trans isomerization rate constant k_i were estimated as ~1 × 10^{-2} and ≤1 × 10^{-6} sec^{-1} at 25° from initial slopes (k_H and ($k_H + k_i$), respectively). For *trans*-$Cr(en)_2(ONO)OH^+$ first-order ONO^--release rate plots at 333 nm were linear and of the same slope in pH 11.5 buffers. This was unexpected in view of the different course of substitution at pH 10.0 and 11.5 indicated by overall spectral changes. While it is possible that the formation of OH^- ion pairs differing in course but not rate of substitution could explain such behavior, it is also possible that a much more complex reaction scheme could apply. As presently understood, however, the reactions of the *cis*- and *trans*-$Cr(en)_2(ONO)_2^+$ systems in en buffers may be summarized by the scheme of Figure 6.

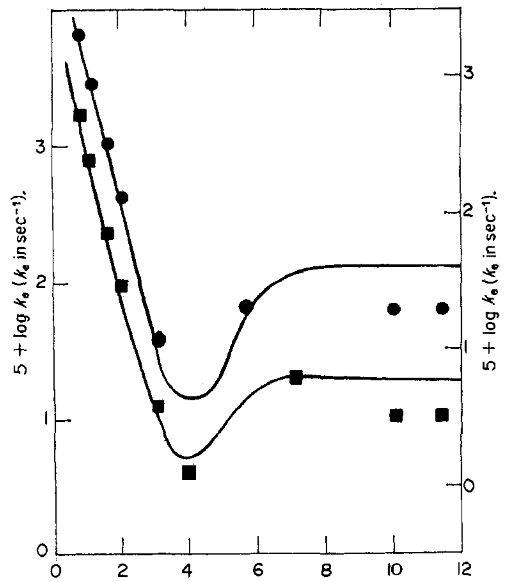

Figure 5.—Dependence of rate of ONO^- loss from equilibrium mixture of $Cr(en)_2(ONO)OH_2^{2+}$ and $Cr(en)_2(ONO)OH^+$ on pH (I = 0.15 *M*) at 25.3°: upper curve (right-hand ordinates), cis isomers; lower curve (left-hand ordinates), trans isomers.

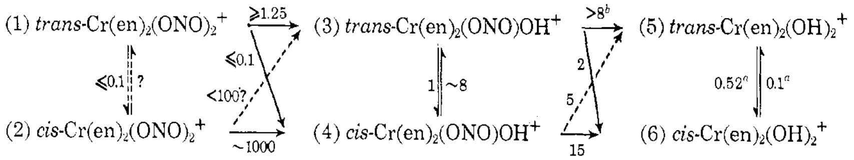

Figure 6.—First-order rate constants (10^5k, $\sec^{-1}$) for hydrolysis and isomerization of chromium(III)–nitrito species in pH 10–11.8 ethylenediamine buffers at 25°. Reactions are best considered as aquations with OH_2 the entering group; the latter is then instantly deprotonated to form the hydroxo species. ^{a} See ref 11b. ^{b} The value given is for pH 10.0; at pH 11.8, $k_{35} \approx 10$.

^{18}O Experiments.—Overall, the pH dependence of ONO^- release from $Cr(en)_2(ONO)X^{n+}$ species is such that at most two reaction paths need be postulated. That is, below pH ~4 a path producing a first-order dependence of rate on $[H^+]$ becomes increasingly important, while above this pH a path giving a pH-independent rate is predominant. As a test of this simple description, ^{18}O-labeling measurements of bond-fission positions under extreme conditions were carried out. By isolating the anhydrous halide salts of aquo complexes produced by reaction with concentrated HCl in ^{18}O-enriched H_2O, it was hoped to examine ^{18}O incorporation for the acid-dependent path alone, and by determining the O isotope composition of ONO^- released in ^{18}O-enriched 0.1 *F* NaOH the acid-independent path might be characterized.

Initial experiments on the incorporation of ^{18}O into several $[Cr(en)_2(OH_2)X]Cl_n$ complexes gave ambiguous results. Thus, after allowing 15 min at 0° for reaction before precipitation, 50–100% incorporation was found. This could result either from Cr–O bond fission in substitution or from $Cr-OH_2$ exchange after formation (or both). To resolve this, experiments were run in which *trans*-$Cr(en)_2(ONO)_2^+$ was allowed to react for various known times and the time dependence of ^{18}O incorporation into the *trans*-$[Cr(en)_2(OH_2)_2]Cl_3$ product was then measured. Although this provided rather badly scattered data (possibly because complete precipitation was not instantaneous), it was possible to extrapolate to an initial ^{18}O content equal to the natural ^{18}O abundance (0.2%) thus indicating that acid-catalyzed hydrolysis occurs with complete Cr–O bond retention. Additional support for this conclusion was found in the variation with X of the extent of ^{18}O incorporation by *trans*-$[Cr(en)_2(OH_2)X]Cl_2$ after 15 min. The extent of ^{18}O incorporation varied in the order $X^- = F^- < Cl^- < Br^-$, which is consistent with what might be expected for the relative OH_2 exchange rates.[19,22]

Unequivocal results were obtained for the incorporation of ^{18}O into ONO^- released from *cis*-$Cr(en)_2(ONO)_2^+$ in $^{18}OH^-$ at *ca.* 20°. Since free NO_2^- does not exchange O with H_2O at high pH,[20] the O isotope composition of N_2O formed from this NO_2^- should reflect the nature of the substitution process. The ^{18}O content of such N_2O, calculated from the relation[23] % $^{18}O = 100R$ = intensity ratio $46 \times 100(44 + 45 + 46)$, was in all cases within experimental error of natural abundance, so that the nonacid-catalyzed hydrolysis can be regarded as a normal Cr–X aquation reaction involving cleavage of the Cr–X bond (here the Cr–O bond).

Discussion

Acid-Catalyzed Reactions.—An experimental rate law of the form $k_e = k_H[H^+]$ does not reveal whether proton transfer or breakup of the protonated substrate is the rate-determining step. The resolution of this ambiguity has indeed been an essential feature of many kinetic studies of basic metal complexes, and since the application of the latter possibility to $Co(en)_2F_2^+$ hydrolyses,[24] it has been taken as paradigmatic for a large number of similar systems. In the case of a metal complex of a polyatomic ligand containing two or more nonequivalent protonation sites, however, it has been recognized[2,25] that proton transfer between two sites within the complex could be rate determining, thus confusing such a dichotomy. Obviously, this possibility must be considered in the case of metal nitrite complexes. Further, if proton transfer to or within a nitrito complex is not rate determining, the well-established formation rate laws[23,26,27] for such species suggest that reaction should, over some acidity range, exhibit autocatalysis by released nitrite. There is, then, a complex context within which to consider acid-catalyzed Cr–ONO hydrolyses.

The present results appear to be the only ones available on Cr–ONO systems which cover acidities where NO_2^- released would not be essentially completely converted to HONO while acid-catalyzed reaction paths are still detectable (*i.e.*, at pH *ca.* 3–4). While autocatalysis was not observed, experimental difficulties make it probable that such an effect could have gone undetected. However, were its absence to be real, at least two possibilities remain: rate-determining proton transfer to and within the complex and protonated complex, respectively. A general acid catalyzed reaction (transfer to complex) would require reaction at higher acidities to occur *via* a path involving HONO, although experimental conditions in the present and other[3,28] studies of Cr–ONO systems would have obscured any such effect. However, on the basis of the improbability of a termolecular reaction, the observations by Matts and Moore[3,28] of rate law terms for $Cr(NH_3)_5ONO^{2+}$

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[22] D. E. Bracken and H. W. Baldwin, Abstracts, 153rd National Meeting of the American Chemical Society, April 1967, No. L 127.

[23] R. K. Murmann and H. Taube, *J. Amer. Chem. Soc.*, **78**, 4886 (1956).

[24] F. Basolo, W. R. Matoush, and R. G. Pearson, *ibid.*, **78**, 4883 (1956).

[25] T. P. Dasgupta and G. M. Harris, *ibid.*, **90**, 6360 (1968).

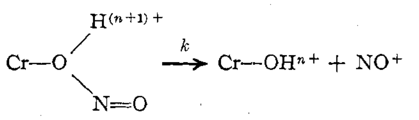
[26] R. G. Pearson, P. M. Henry, J. G. Bergmann, and F. Basolo, *ibid.*, **76**, 5920 (1954).

[27] F. Basolo and G. S. Hammaker, *Inorg. Chem.*, **1**, 1 (1962).

[28] T. C. Matts and P. Moore, *J. Chem. Soc. A*, 1997 (1969).

and $Cr(OH_2)_5ONO^{2+}$ involving $[H^+]^2$ argue against this mechanism. In fact, unless the nitritio N atom of Cr–ONO may act as a protonation site or the remote oxygen may be doubly protonated, these observations also conflict with a slow intracomplex proton-transfer mechanism. The standard specifiic acid catalyzed scheme already applied to $Cr(NH_3)_5ONO^{2+}$ and $Cr(OH_2)_5ONO^{2+}$ then seems to offer the simplest viewpoint for any rationalization of the data of Table III.

A general feature of this table is the rough grouping of $\Delta H^{\ddagger}$ values in accord with the charge of the substrate. Thus, for the 1+ complexes, $\Delta H^{\ddagger}$ lies in the range 20.3–24.3 kcal mol^{-1}, and for the 2+ complexes, $\Delta H^{\ddagger}$ is in the lower range 19.7–20.1 kcal mol^{-1}. While this distinction is not sharp in view of the experimental errors, it is what would be expected on the basis of a rate-determining reaction step (eq 6) where increased



$$\mathrm{Cr{-}O}\begin{matrix}\diagup\mathrm{H}^{(n+1)+}\\ \diagdown\mathrm{N{=}O}\end{matrix} \xrightarrow{k} \mathrm{Cr{-}OH}^{n+} + \mathrm{NO}^{+} \qquad (6)$$

positive charge on $Cr{-}OHNO^{n+}$ would be expected to facilitate the loss of positively charged NO^+. This conclusion, of course, assumes that the charge dependence of $\Delta H^{\ddagger}$ for the protonation preequilibrium is negligible (since under the assumed mechanism k_H of Table III becomes equal to k/K_a, where K_a is the acidity constant of $Cr{-}OHNO^{n+}$). While there is no direct evidence for this supposition, it would not be expected that $\Delta H^{\ddagger}$ for a rate-determining proton-attack mechanism would decrease with increase in substrate charge. Thus, data for the acid-catalyzed hydrolyses of $Cr(en)_2(ONO)X^{n+}$ complexes appear in no way inconsistent with the character and interpretation given by Matts and Moore[3,28] for $Cr(NH_3)_5ONO^{2+}$ and $Cr(OH_2)_5ONO^{2+}$ hydrolyses.

Aquation Reactions.—For the *trans*-$Cr(en)_2(ONO)X^{n+}$ systems where aquation (acid-independent) rate constants for NO_2^- loss could be determined (see Figure 6) or estimated, the relatively low rate of NO_2^- release found is consistent, assuming a dissociative mechanism, with the well-known affinity of Cr(III) for oxygen donors, resulting in a strong Cr–ONO bond. The stereoretentivity of these substitutions is consistent with observations on similar $Cr(en)_2XY^{n+}$ complexes. It is in our qualitative observations on *cis*-$Cr(en)_2(ONO)X^{n+}$, however, that a most remarkable feature of the Cr–ONO system, the cis-labilizing power of the nitrito ligand, is revealed. This is best considered for *cis*-$Cr(en)_2(ONO)Cl^+$. Chloride loss from this cation at 25° is far more rapid than that from *cis*-$Cr(en)_2(NCS)Cl^+$,[5c] *cis*-$Cr(en)_2Cl_2^+$,[5a] and *cis*-$Cr(en)_2(OH)Cl^+$.[29] Likewise (see Figure 6), nitrite loss from *cis*-$Cr(en)_2(ONO)_2^+$ is much faster than from *cis*-$Cr(en)_2(OH)ONO^+$, despite the labilization of many complexes by the presence of a hydroxo ligand. The source of this labilizing ability is not obvious; it could arise from a peculiar steric effect with the coordinated bent nitrito ligand or from unusual solvation properties of the Cr–ONO moiety, as well as from a more conventional π-donor electronic effect. This last possibility may perhaps be ignored since aquation of the X ligand of $Cr(en)_2(ONO)X^{n+}$ ($X^- = Cl^-, ONO^-$) seems to be completely stereoretentive.

[29] D. C. Olson and C. S. Garner, *Inorg. Chem.*, **2**, 558 (1963).

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The Infrared Spectra of Metal Dithienes

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The infrared spectra of bis(1,2-dimethylethylene-1,2-dithiolato)nickel, -palladium, and -platinum, bis(ethylene-1,2-dithiolato)nickel, and bis(1,2-diphenylethylene-1,2-dithiolato)nickel have been recorded from 1600 to 300 cm^{-1}. Band assignments for in-plane infrared-active vibrations were obtained from normal-coordinate analyses. The nature and possible origin of infrared spectral anomalies are discussed. Bonding in chelate rings was interpreted on the basis of bond stretching force constants.

Introduction

Although the reactivity[1] and electronic structures[2] of metal dithienes have been extensively investigated, relatively little information about their infrared absorption spectra is available. Where band assignments have been made,[3] these were empirically deduced and only one or two bands were discussed in detail. Studies of the electronic spectra and structure of the molecular orbitals of metal dithienes[4] have indicated that these complexes possess novel delocalized systems.

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[1] G. N. Schrauzer, *Transition Metal Chem.*, **4**, 299 (1968).

[2] G. N. Schrauzer, *Accounts Chem. Res.*, **2**, 72 (1969).

[3] G. N. Schrauzer and V. P. Mayweg, *J. Amer. Chem. Soc.*, **87**, 1483 (1965).

[4] G. N. Schrauzer and V. P. Mayweg, *ibid.*, **87**, 3585 (1965).