presence of metal ions known to catalyze free-radical decompositions.[6]

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CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
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Kinetics of Aquation of *trans*-Dibromobis(ethylenediamine)chromium(III) Cation

BY ANITA M. WEINER[1] AND JOHN A. MCLEAN, JR.

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A considerable amount of kinetic data has been reported for the aquation of *cis*- and *trans*-dihalobis(ethylenediamine)cobalt(III) cations of the type $[Co(en)_2X_2]^+$ where X = F, Cl, or Br.[2] It has been of recent interest to compare these data with the aquation rates of corresponding chromium(III) complexes. To date the only three chromium analogs which have been studied are the *cis*-difluoro-,[3] *cis*-dichloro-,[4] and *trans*-dichlorobis(ethylenediamine)chromium(III)[5] cations. The paucity of kinetic data on chromium complexes of this type is undoubtedly related to the difficulties encountered in their preparation. In the present study we have attempted to extend knowledge in this area of coordination compounds by determining the pseudo-first-order rate constant and activation constants for the first step aquation of *trans*-dibromobis(ethylenediamine)chromium(III) cation, represented by the equation

$$trans\text{-}[Cr(en)_2Br_2]^+ + H_2O \longrightarrow [Cr(en)_2(H_2O)Br]^{+2} + Br^-$$

Experimental

trans-$[Cr(en)_2Br_2]_2S_2O_6$ was prepared according to the method of Pfeiffer.[6] The dithionate salt was converted to *trans*-$[Cr(en)_2Br_2]Br$ by triturating several times with concentrated HBr and drying overnight at 110°. The possibility of contamination of the bromide by dithionate was ruled out by observing the disappearance of the dithionate absorption band at 1250 cm.$^{-1}$ on a Beckman IR-5 spectrophotometer. Nitrogen was determined in this laboratory by Kjeldahl microanalysis. The remaining elements were also determined by microanalysis.[7] *Anal.* Calcd. for *trans*-$[Cr(en)_2Br_2]Br$: C, 11.67; H, 3.92; Cr, 12.63; Br, 58.25; N, 13.59. Found: C, 11.83; H, 3.68; Cr, 12.10; Br, 57.90; N, 13.46.

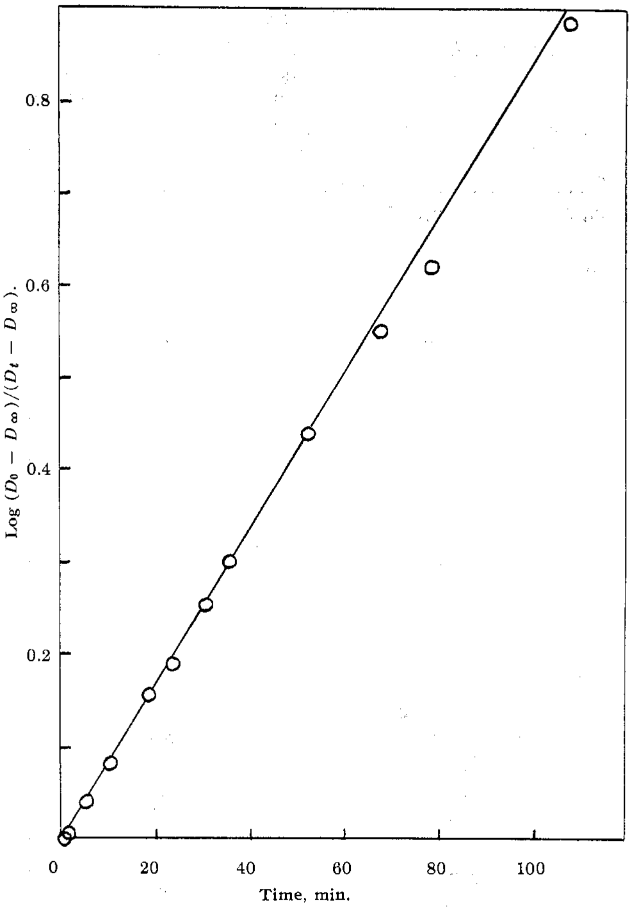

Fig. 1.—Data from a typical kinetic run at 25° in 0.1 *M* HNO_3.

Spectrophotometric data were obtained *in situ* using a Beckman DU spectrophotometer equipped with 1-cm. quartz cells. Temperature was maintained constant within ±0.04° by a thermostatically controlled constant temperature bath. A wave length of 610 mμ was selected for the spectrophotometric study since, at this wave length, there is a maximum difference in the molar absorbency indices of reactant (~34) and product (~9). A sufficient quantity of the salt for a 0.01 *M* solution was quickly dissolved in 0.1 *M* HNO_3, prewarmed to 25°. During the first 80 min., readings were taken at approximately 5-min. intervals and the final reading, D_∞, was recorded at a time corresponding to 10 half-lives. Samples were prepared for study at lower temperatures by quickly dissolving the salt in precooled 0.1 *M* HNO_3 and immediately filtering the solution. Readings were taken at constant intervals over 2–3 half-lives and the final reading again corresponded to the 10 half-life value.

Results and Discussion

Pseudo-first-order rate constants were obtained from the slope of plots, $kt = 2.303 \log (D_0 - D_\infty)/(D_t - D_\infty)$, as illustrated in Fig. 1. Rate plots were linear over 2 half-lives. In previous studies of this type, a positive deviation from linearity of the initial slope was observed after 1–2 half-lives due to interference of the second aquation step.[4,5b] No such deviation was observed in either the spectrophotometric or titration (*vide infra*) data obtained in this study. The value reported in Table I is an average of all runs at 25°.

The relative rates in Table I are in accord with the lower activation energy for the chromium complex. It was found that the rate constant for the aquation

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[1] Taken from the M.S. thesis submitted by Anita M. Weiner to the University of Detroit, 1964.

[2] For a review see D. R. Stranks in J. Lewis and R. G. Wilkens, Ed., "Modern Coordination Chemistry," Interscience Publishers Inc., New York, N. Y., 1960, p. 78.

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

[4] J. Selbin and J. C. Bailar, Jr., *ibid.*, **79**, 4283 (1957).

[5] (a) R. G. Pearson, R. A. Munson, and F. Basolo, *ibid.*, **80**, 504 (1958); (b) D. J. MacDonald and C. S. Garner, *J. Inorg. Nucl. Chem.*, **18**, 219 (1961).

[6] P. Pfeiffer, *Z. anorg. allgem. Chem.*, **56**, 287 (1907).

[7] Microanalysis by Weiler and Strauss; Microanalytical Laboratory, Oxford, England.

TABLE I

RATES OF ACID HYDROLYSIS IN 0.1 M HNO_3 AT 25°

Complex	10^4k, sec.$^{-1}$	E^*, kcal.	ΔS^*, cal./deg.
trans-$[Co(en)_2Br_2]^+$	1.40[a]	26[a]	+9[a]
trans-$[Cr(en)_2Br_2]^+$	3.26	22.4	−1.38

[a] F. Basolo, W. R. Matoush, and R. G. Pearson, *J. Am. Chem. Soc.*, **78,** 4883 (1956).

was independent of acid concentration over the pH range 0.3–1.0. The limited solubility of the reactant prevented extending the pH range to more concentrated acid. The rate constant at 25°, in 0.1 M HNO_3, was checked independently by the potentiometric titration of liberated bromide ion with silver nitrate. Values obtained by both methods agreed within the limits of experimental error.

Arrhenius parameters for this study were calculated from a linear plot of log k *vs.* $1/T$ over the range 14.6–25°. The rate constants determined over this range are given in Table II.

TABLE II

EFFECT OF TEMPERATURE ON THE RATE CONSTANT

Temp., °C.	10^4k, sec.$^{-1}$
14.6	0.837
19.3	1.51
25.0	3.26

It would be presumptuous to choose a mechanism on the basis of the limited data obtained in this investigation. A complete characterization of all species in the reaction mixture, their configurations, and rates of isomerization are required to understand the mechanism of acid hydrolysis reactions.[8]

(8) C. S. Garner and D. J. MacDonald in "Advances in the Chemistry of the Coordination Compounds," S. Kirschner, Ed., The Macmillan Co., New York, N. Y., 1961, p. 267.

CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
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Oxygen Atom Transfer in the Oxidation of Aqueous Chromium(II) by Hydrogen Peroxide[1]

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Hydrogen peroxide rapidly oxidizes aqueous chromium(II) to chromium(III) in acidic solutions. However, the reaction is not simple; monomeric and dimeric chromium(III) species are produced. From an oxygen isotope dilution study, we have obtained information about the path leading to formation of the monomeric chromium(III). We find that one oxygen atom in the water bound to this nonlabile hexaaquochromium(III) is derived from hydrogen peroxide.

The purple solutions resulting from the oxidation of chromium(II) perchlorate by hydrogen peroxide contain a green species in addition to the main product, which is violet hexaaquochromium(III) ion. The fraction of the green form of chromium(III) apparently increases with the speed of mixing and with the concentrations of the reactants, but no systematic investigation of the influences of these parameters has been made. In concentrated solutions under conditions of rapid mixing in a flow apparatus, as much as half of the total chromium has been obtained as the green species, which resembles dimeric oxygen-bridged chromium(III).[2,3] The observation suggests a complex reaction scheme, which may involve competing reactions.

Experimental

Chemicals.—Chromous perchlorate was prepared by electrochemical reduction of chromium(III) perchlorate at a mercury cathode, under nitrogen. Chromium(III) perchlorate was obtained on reduction of chromium trioxide with hydrogen peroxide. Water approximately 1.5% as H_2O^{18} was obtained from Stuart Oxygen Company.

Chromium solutions were analyzed spectrophotometrically. Perchlorate was determined gravimetrically as tetraphenylarsonium perchlorate. Solution densities were obtained from weights of measured volumes of the liquids.

Procedure.—All solvent water was enriched in H_2O^{18}, while hydrogen peroxide was of ordinary isotopic composition. Thus, peroxide oxygen was labeled relative to its H_2O^{18}-enriched solvent environment. Oxygen-18 exchange between water and hydrogen peroxide is a very slow process in acidic solutions.[4]

Reactant solutions containing chromous perchlorate and those containing hydrogen peroxide were separately enriched to the same known mole fraction of H_2O^{18} before they were mixed. The solutions were combined and mixed under vacuum with stirring or in a rapid flow apparatus under direct piston pressure. About 50% stoichiometric excess of hydrogen peroxide was used in each case.

Each final solution containing chromium(III) species was added to concentrated ammonium acid fluoride solution. Only violet hexaaquochromium(III) fluoride precipitates, so that its separation from the green form of chromium(III) is straightforward. The violet salt was washed with alcohol and dried at room temperature in a vacuum desiccator. Two-thirds of the water of hydration was removed from the crystalline salt by pyrolysis in nitrogen at 110°. This water was collected in a vacuum trap. Hydrate water and solvent water samples were isotopically equilibrated with carbon dioxide; the isotope ratio $CO^{16}O^{18}$/total CO_2 was determined on a mass spectrometer. This isotope ratio and the ratio for nonenriched CO_2 are combined with the known constant for the CO_2^{16}–H_2O^{18} exchange equilibrium to obtain the mole fraction of H_2O^{18} in the original water sample.[5]

The above procedure was also carried out with chromium(III) directly (peroxide absent) as an independent check of the method. In other experiments, ferric perchlorate was substituted for hydrogen peroxide as oxidizing agent. Duplicate runs were made in several cases, with one rapid mixing and one slow mixing experiment in each pair.

Results

Results of the isotope dilution experiments and calibration runs are shown in Table I. The first two experiments utilized hexaaquochromium(III) perchlorate which had been equilibrated with H_2O^{18}-enriched solvent for several months. The mole fraction of H_2O^{18}

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(1) From the Ph.D. Thesis of L. B. Anderson, Cornell University, Sept., 1961. Present address: Lockheed Missiles and Space Company, Palo Alto, Calif.

(2) M. Ardon and R. A. Plane, *J. Am. Chem. Soc.*, **81,** 3197 (1959).

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(4) O. L. Forchheimer and H. Taube, *J. Am. Chem. Soc.*, **74,** 3705 (1952).

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