whether electron transfer to the silver acetate could produce acetamide. None was found. Uranium(IV) acetate was 50% ammonolyzed in 30 days while both dioxouranium(VI) acetate and ammonium dioxotris(acetato)uranate(VI) required 130 days.

Since the oxidation reaction is much faster than the ammonolysis reaction, it is concluded that the acetamide produced in the oxidation reaction results from acetate involved in oxygen atom transfer to form the dioxouranium (VI) species. Following this, additional acetamide is formed by the ammonolysis of acetate attached to U(VI).

We may now write equations for the reactions involved. For the oxidation reaction we suggest

$$4NH_3 + 2AgC_2H_3O_2 + U(C_2H_3O_2)_4 = (NH_4)_2UO_2(C_2H_3O_2)_4 + 2CH_3CONH_2 + 2Ag \quad (1)$$

The ammonolysis reaction may be written

$$2(NH_4)_2UO_2(C_2H_3O_2)_4 + 6NH_3 = (NH_4)_2U_2O_7 + 8CH_3CONH_2 + 5H_2O \quad (2)$$

To account for all of the acetamide formed, we have suggested that the complex $(NH_4)_2UO_2(C_2H_3O_2)_4$ may have been present in solution. There is ample precedence for this kind of complex. The compounds $UO_2(C_2H_3O_2)_2\cdot 2HC_2H_3O_2\cdot 2H_2O$,[4] $ZnUO_2(C_2H_3O_2)_4$,[5] and $((CH_3)_4N)_2UO_2(C_2H_3O_2)_4$[5] have all been reported to contain four coordinated acetate groups. Apparently, ammonium acetate is easily lost by this complex to give the tris complex $(NH_4)UO_2(C_2H_3O_2)_3$, which was actually isolated.

Acknowledgment.—We are indebted to the Atomic Energy Commission for support under Research Grant AT(11-1)-362.

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[4] A. Colani, *Bull. Soc. Chim. France*, [4] **35**, 1305 (1924).

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A Study of the Decomposition of Peroxochromic Acid

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Received September 27, 1965

Peroxochoromic acid undergoes a first-order decomposition to Cr(III) ion with the liberation of O_2. Several researchers have observed that oxygen evolution continues for a period of time after the blue peroxochromic acid is lost.[1,2] It is interesting to note that those workers who have studied the decomposition reaction have centered their studies on the loss of peroxochromic acid and not on the rate of formation of Cr(III) ion. Since the chromium is undergoing a three-electron change and the peroxide a two-electron change, it is more than likely that one or more intermediates will be present during the decomposition.

The mechanism of this decomposition was studied with the aid of dipicolinic acid (DPA), $C_5H_3N(COOH)_2$, as a chelating agent to interrupt decomposition by stabilizing any intermediate(s).

Experimental Section

Reagents.—H_2O_2 (30%) diluted to 0.933 *M* was used. The H_2O_2 solution was standardized using acidified KI solution and titrating the I_2 liberated with $Na_2S_2O_3$ solution. The $Na_2S_2O_3$ was previously standardized against a mixture of KI and KIO_3. Starch was the indicator in both standardizations.

A 60% solution of reagent grade $HClO_4$ diluted to 1.0 *M* was used. Reagent grade $K_2Cr_2O_7$ was used for all kinetic runs and for the spectrophotometric standardization of the $Cr(ClO_4)_3$ solutions. It was dried overnight at 110–120°.

Sulfate-free $Cr(ClO_4)_3$ was obtained from K & K Laboratories, Inc., and was >99.95% pure. Solutions of $Cr(ClO_4)_3$ were analyzed by oxidizing the Cr(III) ion to $Cr_2O_7^{2-}$ and comparing their absorbancies with reagent grade, acidified $K_2Cr_2O_7$ solutions using a Beckman Model DU spectrophotometer.

The dipicolinic acid used was obtained from K & K Laboratories, Inc., and after recrystallization was >98% pure.

Oxygen Evolution.—The quantity of oxygen liberated and its rate of liberation by the peroxochromic acid decomposition was determined manometrically. The thermostated reaction vessel consisted of a bulb with a movable side arm. The bulb contained acidified potassium dichromate (pH 1), and the side arm contained hydrogen peroxide. Reaction was initiated by turning the jointed side arm so that its contents emptied into the bulb. The concentrations of $K_2Cr_2O_7$ and H_2O_2 were 1.00×10^{-3} and 0.882 *M*, respectively. Runs were made with and without DPA being added to the original reaction mixture. The concentration of DPA was 1.0×10^{-2} *M*. The temperature was 18.7°.

Stoichiometry of the Chelate.—Job's method of continuous variation[3] was used to determine the formula of the chelated intermediate. Absorbancies of the various solutions were measured at 540 mμ using a Beckman Model DU spectrophotometer.

Charge of Chelated Intermediate.—A cation-exchange resin Amberlite IR-120 and an anion-exchange resin Amberlite IRA-400 were used to determine whether the chelated intermediates were positively or negatively charged. The columns were regenerated using a 5% $HClO_4$ solution.

Kinetics of Intermediate Ion Loss.—A 90.0-ml portion of an acidified solution of 1.09×10^{-3} *M* $K_2Cr_2O_7$ and 10.0 ml of 0.933 *M* H_2O_2 solution were mixed to initiate the reaction. The initial pH of the solution was 1.00. After mixing, 5.00-ml aliquot portions were removed from the reaction mixture at designated intervals and added to flasks containing 10.0 ml of 0.0100 *M* DPA. The quantity of DPA used gave a molar ratio for DPA : Cr of 10 : 1. This excess was used to ensure a rapid and complete conversion of the intermediate to the chelated intermediate. Excess hydrogen peroxide and acid were used so that the order of the reaction would be in terms of the intermediate only. Absorbancies of the chelate formed were measured immediately.

Results and Discussion

DPA reacted very slowly with Cr(III) ion from any Cr(III) salt, *i.e.*, $Cr(ClO_4)_3$ or $Cr_2(SO_4)_3$. In order for the chelation to occur rapidly, the solution had to be boiled. The chelation then occurred in <1 min as com-

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[1] F. Gnadinger, *Z. Physik. Chem.* (Leipzig), **206**, 63 (1956).

[2] M. Bobtelsky, A. Glasner, and L. Bobtelsky-Chakin, *J. Am. Chem. Soc.*, **67**, 966 (1945).

[3] W. C. Vosburgh and G. R. Cooper, *ibid.*, **63**, 437 (1941).

pared to the several days it takes if the reaction is allowed to occur at room temperature. When the DPA was added to the reaction mixture of acidified hydrogen peroxide and potassium dichromate, chelation of the product was rapid, occurring within a few seconds at room temperature. This suggests that an intermediate is formed in the reaction scheme that is more reactive with DPA than is hexaaquochromium(III) ion.

Oxygen Evolution.—The quantity of oxygen liberated through the reduction of potassium dichromate was severely curtailed by the addition of DPA to the original reaction mixture. The quantity of oxygen liberated with DPA present was one-fourth to one-third less than that without the DPA present in a time interval of about 1 hr, which is sufficient for the reaction without DPA to be completed at room temperature. This latitude of about 8% was introduced because of the slight dependence of the quantity released on the rate of shaking of the reaction mixture. It was observed however that the rate of O_2 liberation during the first 3 to 4 min was the same whether or not the DPA was present. It was also observed that addition of DPA did not affect the time it took for the characteristic blue color of perchromic acid to be lost. These facts were interpreted to mean that the DPA does not react with CrO_5 but rather with a product of its decomposition.

Spectra of Immediately Formed and Aged Chelate.—The absorption curves obtained on the immediately formed chelated product, on the chelated product after standing for 2 days (aged chelate), and on a chelated Cr(III) ion obtained by boiling a solution of chromic perchlorate with excess DPA at pH 1.0 are given in Figure 1. It is observed that the spectrum of the aged chelate is identical with that of the chelated Cr(III) ion. Comparison of the spectrum of the aged chelate with that of the immediately formed chelate shows that they are qualitatively similar throughout the visible region. There is, however, a shift of about 25 mμ toward the red as the product ages. Owing to the similarity of the spectra, we feel it reasonable to assume that the chromium was in the +3 oxidation state in both the immediately formed chelate and the aged chelate. The difference in spectra was caused by the dipicolinic acid stabilizing a peroxide-containing chromium intermediate. This is not unreasonable since the quantity of oxygen liberated is reduced by the presence of DPA, indicating that an oxygen-containing species is being stabilized. Over the course of several days however this chelated peroxide intermediate slowly decomposed, yielding the chelated Cr(III) ion. If this intermediate did contain a chromium in the +3 oxidation state, then there must also have existed a very unstable reactive intermediate containing Cr(IV) since one mole of O_2^{2-} would reduce one mole of Cr(VI) to Cr(IV).

Stoichiometry of the Chelate.—Cr(III) combines with either one or two dipicolinate ions depending upon the pH of the solution. For pH values equal to or less than 1, the chelate formed is 1:1. For pH values greater than 2, the chelate is 1:2. Hartkamp[4] used Job's method of continuous variations to determine the stoichiometry of the chelation. At pH values between 1 and 2, both chelates may exist. The 1:2 chelate had its maximum molar absorptivity at a wavelength of 550 mμ; the 1:1 chelate, at 565 mμ. The spectra of our immediately formed chelate and the corresponding aged chelate were obtained for three different Cr:DPA ratios—7:3, 1:1, and 3:7—and at pH values between 1 and 2. The maximum in the spectrum of the immediately formed chelate was the same regardless of the Cr:DPA ratio and the pH (Figure 1). The same is true for the aged chelate. The immediately formed chelated intermediate proved to be a 1:1 chelate through use of Job's method. The aged chelate, with its maximum at 565 mμ, also was 1:1 as it agreed with Hartkamp's work. That a 1:1 chelate was formed immediately, instead of a 1:2 chelate, is quite reasonable since the presence of a complexed peroxide group would prevent the chelation of a second tridentate ligand.

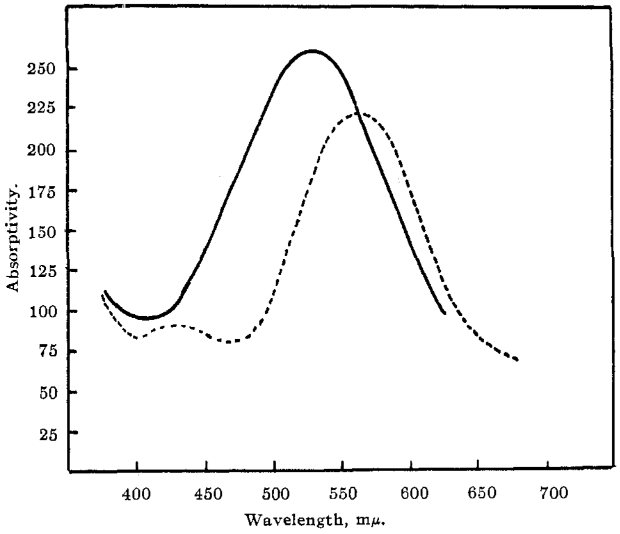

Figure 1.—Absorption curves for immediately formed chelate (———) and for aged chelate and chelated Cr(III) (– – – –).

Charge of Chelated Intermediate.—If the immediately formed chelate did contain one peroxide group, then the ion would have a single negative charge. After standing for 2 days, if the peroxide was lost and was replaced by one or two water molecules depending upon whether the peroxide was a monodentate or bidentate ligand, the ion would then assume a single positive charge. Whether or not this change of charge occurred was determined using a cation- and an anion-exchange resin. The solution was initially 6.87×10^{-3} *M* in $K_2Cr_2O_7$, 3.7 *M* in H_2O_2, 1.19×10^{-2} *M* in DPA, and 5.70×10^{-2} *M* in $HClO_4$. When the immediately formed chelate was passed through both columns set up in parallel, it was found to exchange 100% with the anion-exchange column and not at all with the cation-exchange column. The aged product was found to exchange to the extent of 80% with the cation-exchange column. The exchange only showed that the immediately formed chelate had a negative charge,

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(4) H. Hartkamp, *Z. Anal. Chem.*, **187**, 16 (1962).

whereas the aged chelate had a positive charge. If the oxidation state of the chromium in the chelated intermediate was +4 as was suggested by Beck and Bardi,[5] then the immediately formed chelate would have a zero charge on it and would not exchange with either exchange column. That there was 80% exchange of the aged chelate instead of 100% might be in part due to dimerization, which, if it did occur, would yield a neutral species. This has not yet been investigated. The unchelated, colorless intermediate, that is, the species following the loss of blue perchromic acid without DPA added, was passed through both columns and was found to exchange with the cation- and not the anion-exchange column. This was shown by adding DPA to the solution immediately after passing through the columns. The characteristic color of the chelated intermediate was obtained only from the solution which passed through the anion-exchange column.

Kinetics of the Loss of the Reactive Intermediate.—The loss of the reactive intermediate was followed by removing aliquot portions of the original reaction mixture (no DPA present) at specified time intervals and adding it to solutions containing a tenfold excess of DPA to ensure rapid and complete conversion of the reactive intermediate to the chelated form. The absorbance of these solutions was then immediately measured to prevent the slow chelation of $Cr(H_2O)_6^{3+}$ from interfering. The concentrations of the reactive intermediate and the hexaaquochromium(III) ion were determined from the equations

$$C^* = \frac{A_T - \epsilon Q l}{(\epsilon^* - \epsilon) l} \qquad C = Q - C^*$$

where C and C^* are the concentrations of hexaaquochromium(III) ion and reactive intermediate, respectively (which is equal to the concentration of chelated intermediate); ϵ and ϵ^* are the molar absorptivities of the hexaaquochromium(III) ion and of the chelated reactive intermediate, respectively; Q is the total chromium concentration; l is the cell length; A is the absorbance at a wavelength of 540 mμ. The values of ϵ and ϵ^* were determined to be 27.0 and 270, respectively, at 540 mμ.

The reaction, run in excess hydrogen ion and hydrogen peroxide, was found to be second order with respect to reactive intermediate (Figure 2). The pH did not change appreciably during reaction, the initial value being 0.98 and the final value 1.07. Duplicate runs were made at each of three temperatures, and an activation energy of 15.0 kcal/mole was found. The rate constants (M^{-1} sec^{-1}) are as follows: at 28.5° (1) 5.66, (2) 5.58; at 18.7° (3) 2.43, (4) 2.43; at 8.8° (5) 1.01 (6) 0.97.

The following stoichiometric equation for the loss of reactive intermediate is proposed

$$2Cr(O_2)(H_2O)_5^{+} + 4H^{+} \longrightarrow 2Cr(H_2O)_6^{3+} + O_2$$

Whether this is a simple disproportionation of the peroxide groups or is a complex reaction involving a nucleophilic displacement as the rate-determining step has not yet been determined.

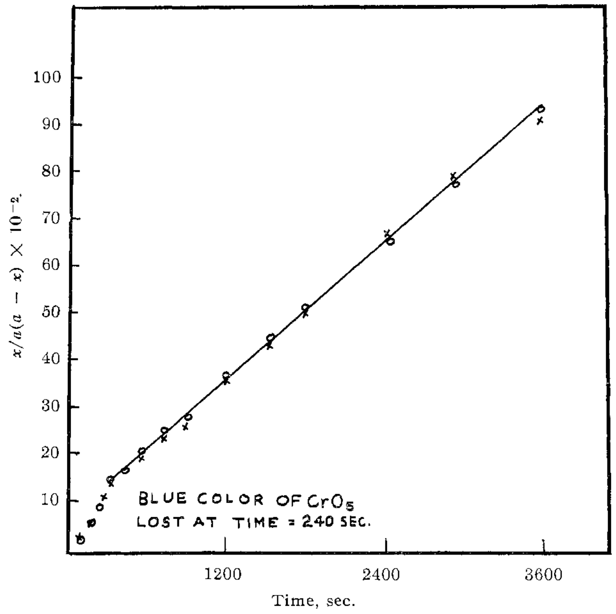

Figure 2.—Second-order plot for intermediate disappearance at 18.7°. Replicate runs are represented by × and O points. The initial pH is 0.98. The initial concentration of peroxochromic acid is a, and the concentration at any time is $a - x$.

Acknowledgment.—Financial support from the National Science Foundation Undergraduate Research Participation Program is gratefully acknowledged.

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[5] M. T. Beck and I. Bardi, *Acta Chim. Acad. Sci. Hung.*, **29**, 283 (1961).

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Vibrational and Electronic Spectra of Hexanitrocobalt(III) Salts

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Received October 19, 1965

Salts of the hexanitrocobalt(III) anion have been known for many years. Recently Schutte[1] has investigated the infrared spectra of several such salts; however, Schutte's work covered only the rock salt region. The spectrum in the cesium bromide region, where many metal–ligand vibrations absorb, was not reported. Nakamoto and co-workers,[2] examining nitro and nitrito complexes, assign the Co–N stretching frequency in $K_3[Co(NO_2)_6]$. We have observed the infrared spectrum of $Na_3[Co(NO_2)_6]$ to be different from that reported by Nakamoto, *et al.*, for the analogous potassium salt. This has led us to examine the spectra of a number of

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[1] C. J. H. Schutte, *Z. Anorg. Allgem. Chem.*, **334**, 304 (1965).

[2] K. Nakamoto, J. Fujita, and H. Murata, *J. Am. Chem. Soc.*, **80**, 4817 (1958).