The Preparation and Properties of Peroxychromium(III) Species[1]

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Abstract: Two green peroxychromium species have been isolated from chromium(VI)–hydrogen peroxide reaction mixtures in 2–6 *M* perchloric acid. On the basis of the elution rate from cation-exchange resin and the oxidizing capacity, these species are identified tentatively as CrO_2Cr^{4+} and $CrO_2CrO_2Cr^{5+}$, polynuclear species of chromium(III) and peroxide ions. Although decomposition of each of these species follows first-order kinetics, the stoichiometry of decomposition is not simple. Hexaaquochromium(III) ion, hydrogen chromate ion, and oxygen are produced from each of the two species, and hydrolytic polynuclear chromium(III) species are also produced in decomposition of the trimer. Activation parameters for the decomposition reactions are: $Cr_3(O_2)_2^{5+}$, $\Delta H^{\ddagger} = 22.3$ kcal mole^{-1}, $\Delta S^{\ddagger} = -2.3$ cal mol^{-1} deg^{-1}; and $Cr_2O_2^{4+}$, $\Delta H^{\ddagger} = 21.5$ kcal mole^{-1}, $\Delta S^{\ddagger} = -2.3$ cal mole^{-1} deg^{-1}. Cerium(III) and cerium(IV) catalyze the decomposition of the trimer to chromium(VI) and hexaaquochromium(III) ion. The reactions of chromium(II) with oxygen and with chromium(VI) were investigated also.

The net chemical change which occurs when chromium(VI) and hydrogen peroxide react in acidic aqueous solution is

$$2HCrO_4^- + 3H_2O_2 + 8H^+ = 2Cr^{3+} + 3O_2 + 8H_2O$$

It is certain that reaction intermediates are formed in the course of this reaction; their maximum concentrations depend upon the concentration conditions and temperature. One such intermediate is the familiar blue peroxychromium(VI) species $H_2OCrO(O_2)_2$, represented as CrO_5, which is formed in the net reaction[3]

$$HCrO_4^- + 2H_2O_2 + H^+ = CrO_5 + 3H_2O$$

If the reaction of chromium(VI) and hydrogen peroxide is carried out at temperatures less than zero in acidic solution, green cationic species are formed.[4,5] The present paper describes the preparation and properties of two different unstable cationic chromium peroxide species, one of which is that observed by Ardon and Bleicher.[5] Discussion of the present work will assume the species to be a dimeric species $Cr_2O_2^{4+}$ and a trimeric species $Cr_3(O_2)_2^{5+}$, and evidence supporting this interpretation will be presented. Equations for the net reactions in which each of these species is formed from chromium(VI) and hydrogen peroxide are

$$2HCrO_4^- + 4H_2O_2 + 6H^+ = Cr_2O_2^{4+} + 3O_2 + 8H_2O$$

$$6HCrO_4^- + 13H_2O_2 + 16H^+ = 2Cr_3(O)_2^{5+} + 9O_2 + 24H_2O$$

Experimental Methods

Reagents and Equipment. All chemicals used were reagent grade. The water was doubly distilled; between distillations the water was passed through a Barnsted mixed-bed ion exchanger. Acidic solutions of chromium(II) perchlorate were prepared immediately before use by passing a solution of hexaaquochromium(III) perchlorate in 2 *M* perchloric acid through a column containing amalgamated zinc. Spectra were obtained with a Cary recording spectrophotometer (Model 15). For the kinetic runs at 25.5°, the temperature was checked several times during a run, and the variation of temperature was less than 0.2° from 25.5°.

Analyses. Reaction mixtures prepared from chromium(VI), hydrogen peroxide, and perchloric acid may contain hexaaquochromium(III) ion, hydrolytic polymeric chromium(III) species,[6] peroxychromium(III) species, as well as unreacted chromium(VI) or hydrogen peroxide. Analysis of reaction mixtures for these species involved prior separations using column ion-exchange techniques.

A jacketed 25-cm column, 1 cm in diameter, of Dowex 50W-X2 (100–200 or 200–400 mesh) was used. The temperature of the column was maintained near 0° by circulating ice water through the jacket. Unreacted excess hydrogen peroxide or chromium(VI) was washed from the column with 500 ml of 0.1 *M* perchloric acid. The chromium(VI) concentration was determined from its absorption at 372 mμ after making the solution alkaline with sodium hydroxide.[7] The hydrogen peroxide concentration was measured by adding an excess of cerium(IV) and titrating the excess with iron(II). Alternately, an excess of iron(II) was added and the excess titrated with cerium(IV). Results of the two methods agreed. Hexaaquochromium(III) ion was eluted with 500 ml of 2.0 *M* perchloric acid. The concentration was measured spectrophotometrically[7] after oxidation to chromium(VI) with alkaline hydrogen peroxide. The dimeric species, $Cr_2O_2^{4+}$, was eluted with 2 *M* perchloric acid; the trimer, $Cr_3(O_2)_2^{5+}$, was eluted with 5 *M* perchloric acid. The concentrations were measured spectrophotometrically after oxidation to chromium(VI) with alkaline hydrogen peroxide. An elution curve is shown in Figure 1.

In some experiments, the oxidizing normality due to the green peroxychromium(III) species was determined indirectly by treating a sample of unprocessed reaction solution with an excess of iron(II) and titrating the excess with cerium(IV). This titration gave the total oxidizing normality of the solution; the normality due to the peroxychromium(III) species was obtained by subtracting the normality of the chromium(VI) or hydrogen peroxide (whichever was in excess) from the total normality. In some experiments iodide ion was used to determine the total oxidizing normality of the solution; the triiodide ion produced was titrated with thiosulfate. The oxidizing normality as measured in the reaction with iodide ion was found to be slightly larger (up to 4%) than in the reaction with iron(II). The normality measured with iron(II) was assumed to be correct since oxygen interferes less in the iron(II) procedure.

The normality of the eluted $Cr_2O_2^{4+}$ and $Cr_3(O_2)_2^{5+}$ was determined by the iron(II)–cerium(IV) procedure already outlined.

Although there was no evidence for production of the hydrolytic polymeric chromium(III) species in the preparative experiments, there was such evidence in decomposition of the trimeric species

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(2) (a) National Science Foundation Postdoctorate Fellow, 1963–1964; (b) National Science Foundation Summer Research Participant, 1963.

(3) D. F. Evans, *J. Chem. Soc.*, 4013 (1957).

(4) Blue-green species are produced by the reaction of hydrogen peroxide and chromium trioxide in trifluoroacetic acid (G. S. Fugioka and G. H. Cady, *J. Am. Chem. Soc.*, **79**, 2451 (1957)). R. E. Connick (private communication) has observed green species in experiments similar to ours.

(5) M. Ardon and B. Bleicher, *J. Am. Chem. Soc.*, **88**, 858 (1966).

(6) J. A. Laswick and R. A. Plane, *ibid.*, **81**, 3564 (1959).

(7) G. W. Haupt, *J. Res. Natl. Bur. Std.*, **48**, 414 (1952).

Table I. The Yields of the Two Green Species for Different Reactant Concentrations[a]

Initial concn, M[b]		Moles of H_2O_2 consumed/mole of $HCrO_4^-$	% Cr in the products as			% Cr recovered
$[HCrO_4^-]$	$[H_2O_2]$		Cr^{3+}	$Cr_2O_2^{4+}$	$Cr_3O_4^{5+}$	
0.0101	0.0181	1.89	93.1	3.8	2.3	99.2
0.0795	0.149	1.96	89.2	4.6	5.9	99.7
0.566	1.41	2.62	74.2	5.0	16.8	96.0[c]

[a] The final solution was 2.0 M in perchloric acid. The temperature was −9 to −7°. [b] The concentrations the reactants would have had if no reaction had occurred. [c] A third green species was observed in this preparation. This species was not removed from the column.

$Cr_3(O_2)_2^{5+}$. Hydrolytic chromium(III) species were eluted from the ion-exchange column using 0.5 M barium perchlorate–1.0 M perchloric acid in analysis of some aged solutions in which $Cr_3(O_2)_2^{5+}$ had decomposed.

Preparation of the Green Peroxychromium(III) Species. The green peroxychromium(III) species were prepared by reducing chromium(VI) in acidic solution with hydrogen peroxide. In several experiments 10 M hydrogen peroxide was added slowly to a solution which was 1 M in chromium(VI) and 3–6 M in perchloric acid. The temperature was kept between −9 and −4° with a salt–ice bath. Chromium trioxide was usually the source of chromium(VI), but in a few experiments potassium dichromate was used, in which case the precipitated potassium perchlorate was removed before addition of hydrogen peroxide. The hydrogen peroxide was added dropwise for 1–3 hr until only a slight excess of either hydrogen peroxide or chromium(VI) was present. The "end point" was established by measurement of the light absorption of a diluted portion of reaction mixture at 350 mμ where light absorption of chromium(VI) is high relative to that of both the green species and hexaaquochromium(III) ion. In these experiments, the hydrogen peroxide needed to react completely with the chromium(VI) ranged from 2.5 to 3.0 moles of hydrogen peroxide per gram-atom of chromium(VI). The average value obtained in 13 experiments was 2.8. In experiments of this type, between 28 and 53% of the reduced chromium occurred as the green species (the average was 34%); the remainder was hexaaquochromium(III) ion. There was no discernible trend in yield with concentration conditions in these experiments. In most of these experiments the hydrogen ion concentration varied appreciably with occurrence of reaction.

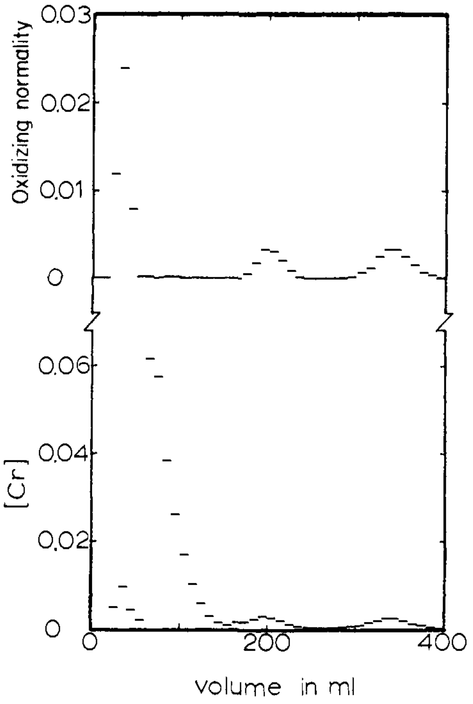

Figure 1. Separation of $HCrO_4^-$, Cr^{3+}, $Cr_2O_2^{4+}$, and $Cr_3(O_2)_2^{5+}$ using Dowex 50W-X2, 200–400 mesh, at 0°. The column was eluted with 250 ml of 2 M perchloric acid followed by 150 ml of 5 M perchloric acid; 98.7% of the chromium was recovered. The number of oxidizing equivalents per chromium atom for a few of the fractions are: 190–200 ml, 1.18; 200–210 ml; 1.13; 210–220 ml, 1.09; 320–330 ml, 1.24; 330–340 ml, 1.29; 340–350 ml, 1.30; and 350–360 ml, 130. An estimate of the elapsed time can be made on the basis of the elution rates: 2 M perchloric acid, 1.0 ml/min; 5 M perchloric acid, 1.3 ml/min.

In other experiments hydrogen peroxide in 2 M perchloric acid was added rapidly (7 to 15 sec) to an equal volume of chromium(VI) in perchloric acid. The final reaction solution was 2 M in hydrogen ion. The temperature of the reactant solution and the reaction mixture was kept between −9 and −7° with a salt–ice bath. The blue color of peroxychromium(VI) was observed for about 15 sec if chromium(VI) was in slight excess but persisted for 75–90 sec if hydrogen peroxide was in slight excess. The color of the solution then changed to green, an observation suggesting that the peroxychromium(III) species are produced from blue peroxychromium(VI). The results of three such experiments are summarized in Table I.

Several attempts were made to prepare green peroxychromium(III) species by treating chromium(II) with oxygen since the dimeric species $Cr_2O_2^{4+}$ is a logical intermediate in the reaction of chromium(II) and oxygen.[8] Air or pure oxygen was bubbled through 125 ml of 2 M perchloric acid at 0°. After the solution was saturated (~15 min), 250 ml of chromium(II) solution (2.9×10^{-4}–0.057 M) was added slowly over a period of 40–90 min. Reaction solutions were analyzed 20–30 min after the chromium(II) had been added. The products formed in the reaction and the range of percentages of the total chromium in each species are: hexaaquochromium(III), 45–67%; chromium(VI), 2–22%; and hydrolytic polymeric chromium species, 0–51%. The cationic green peroxychromium(III) species were not observed. However, a yellow cation with an absorption maximum at 385 mμ was observed. This species decomposed within a few hours at room temperature. The yellow species is possibly one of the species observed by Piccard,[9] who showed that the reaction of chromium(II) and oxygen produced two unstable species in addition to chromium(VI) and chromium(III) species. The relative concentrations of chromium products in the reaction solution are independent of the flow rate of gas (flow rates varied from 21 to 94 ml sec^{-1}), and it is assumed that the solution remained saturated with oxygen during the reaction. The relative yields depend on the oxygen concentration and the rate of addition of chromium(II). When air was used, 2–3% of the chromium(II) was oxidized to chromium(VI) (for four experiments in which the flow rate of air varied from 35 to 79 ml sec^{-1} and the rate of chro-

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[8] This species has been proposed as a reaction intermediate in the reaction of chromium(II) and oxygen (R. W. Kolaczkowski and R. A. Plane, *Inorg. Chem.*, 3, 322 (1964); G. Thompson, Thesis, University of California, Berkeley, June 1964 (University of California Radiation Laboratory Report 11410)). An analogous species is produced in the oxidation of chromium(II) by oxygen in ammoniacal solution (T. B. Joyner and W. K. Wilmarth, *J. Am. Chem. Soc.*, **83**, 516 (1961)).

[9] J. Piccard, *Ber.*, **46**, 2477 (1913).

mium(II) addition varied from 38 to 85 × 10^{-8} mole sec^{-1}). Similar experiments using pure oxygen instead of air resulted in 8–11% of the chromium(II) being oxidized to chromium(VI) (for three experiments with a flow rate of oxygen between 21 and 82 ml sec^{-1} and a chromium(II) addition rate of 53–82 × 10^{-8} mole sec^{-1}). The highest yields of chromium(VI) (~22%) were obtained for a low chromium(II) addition rate (1.8–6.8 × 10^{-8} mole sec^{-1}). As the rate of addition of chromium(II) increases, the yield of chromium(VI) decreases. The yield of chromium(VI) for different chromium(II) addition rates (given as 10^{-8} mole sec^{-1}) are: 22%, 1.78; 22%, 6.75; 15%, 17.2; 18%, 18.5; 11%, 53.1; 10%, 61.9%; 8%, 81.9; 6%, 103; 7%, 103; 2%, 509. Low rates of addition of chromium(II) also cause the higher yields of hexaaquochromium(III) and the unidentified yellow species.

The Reaction of Chromium(II) and Chromium(VI). The observation that oxygen oxidation of chromium(II) under the conditions employed in this study (addition of chromium(II) to the solution of oxygen) produces chromium(VI) suggested the desirability of additional studies of the stoichiometry of the reaction of chromium(II) and chromium(VI). Ardon and Plane studied this reaction and found that ~50% of the chromium(III) produced is present as hexaaquochromium(III) ion and ~50% as hydrolytic dimer.[10] Hegedus and Haim have confirmed this approximate stoichiometry,[11] but their tracer experiments show that reaction does not go exclusively by the sequence of 1-equiv steps proposed by Ardon and Plane. Most of our experiments were performed at concentrations appreciably lower than in the studies cited (0.01 M Cr^{VI}, and 0.03 M Cr^{2+} in ref 11), and the yield of hexaaquochromium(III) ion exceeded 50% in practically all of our experiments. The results of these experiments, all of which were carried out in ~2 M perchloric acid, are (given as temperature, $[Cr^{2+}]_0$, $[HCrO_4^-]_0$, % chromium present in product as hexaaquochromium(III)ion): 25°, 2.8 × 10^{-4}, 1.4 × 10^{-4}, 69%; 0°, 1.2 × 10^{-3}, 6.0 × 10^{-4}, 67%; 0°, 1.4 × 10^{-3}, 6.7 × 10^{-4}, 71%; 25°, 1.4 × 10^{-3}, 5.4 × 10^{-4}, 62%; 25°, 1.4 × 10^{-3}, 6.7 × 10^{-4} 65 ± 3% (average of two experiments with different orders of mixing); 25°, 1.3 × 10^{-3}, 1.3 × 10^{-3}, 69%; 25°, 1.3 × 10^{-2}, 6.8 × 10^{-3}, 55%; 25°, 6.7 × 10^{-2}, 2.7 × 10^{-2}, 54%. Although the results show appreciable scatter, the deviations from 50% are outside of experimental error. The values approach 50% as the concentrations are raised.

Experimental Results

The Oxidizing Capacity of Green Peroxychromium(III) Species. Direct analyses of the separated fractions show that the more easily eluted green species has 1.1 ± 0.1 oxidizing equivalents per chromium atom (the average of 0.90, 0.98, 1.11, 1.13, 1.15, and 1.17; these values are for six independent preparations). The other green species has 1.30 ± 0.04 oxidizing equivalents per chromium atom (the average of 1.26, 1.30, 1.31, 1.32, and 1.32; five independent preparations).

If production of oxygen does not occur when an acidic solution of green peroxychromium(III) species is made alkaline, the oxidizing capacity of the bound peroxide is converted to chromium(VI). Three independent experiments of this type on the more easily eluted species (the dimer) gave 0.99, 1.02, and 1.11 for the number of oxidizing equivalents per gram-atom of chromium. Before determination of the light absorption due to chromium(VI) in these experiments, chromium(III) was separated from the mixture. This was accomplished by acidification and removal of chromium(III) with cation-exchange resin, followed by making the solution alkaline. Analogous experiments on the less easily eluted species (the trimer) gave amounts of chromium(VI) which corresponded to 1.20, 1.26, and 1.29 oxidizing equivalents per gram-atom of chromium.

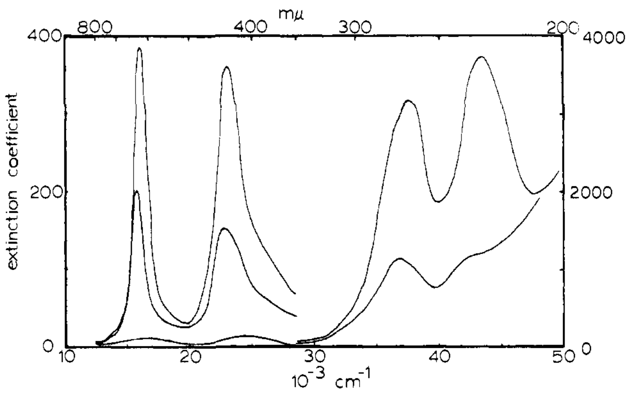

Figure 2. Spectra of $Cr_3(O_2)_2^{5+}$ in 5 M $HClO_4$ (upper curve), $Cr_2O_2^{4+}$ in 2 M $HClO_4$ (middle curve), and $Cr(OH_2)_6^{3+}$ in 2 M $HClO_4$ (lower curve). The spectrum of $Cr(OH_2)_6^{3+}$ is not extended into the ultraviolet region. Absorbancy indices are based on concentration in gram-atoms of chromium per liter. The right-hand ordinate should be used for wavelengths shorter than 350 mμ.

The Tentative Identification of the Peroxychromium(III) Species. On the basis of the rates of elution of the two species and their oxidizing capacity, the species are identified tentatively as $Cr_2O_2^{4+}$ (with an oxidizing capacity of 1.00 unit per chromium atom) and $Cr_3(O_2)_2^{5+}$ (with an oxidizing capacity of 1.33 units per chromium atom). Each species is assumed to contain chromium(III) and peroxide.

Spectra of Peroxychromium(III) Species. The spectra of the two green peroxychromium(III) species, measured soon (<5 min) after elution, are given in Figure 2. Rescanning the spectrum showed no appreciable changes, indicating that inappreciable decomposition had occurred during the spectral measurements. The wavelengths (mμ) and molar absorbancy indices (calculated per gram-atom of chromium) for absorption maxima for $Cr_2O_2^{4+}$ are: 272, 1180; 439, 153; and 634, 202; and for $Cr_3(O_2)_2^{5+}$: 230, 3800; 267, 3170; 433, 360; and 625, 384. The species studied by Ardon and Bleicher[5] has a very similar spectrum to that reported above for $Cr_3(O_2)_2^{5+}$; peaks are located at 230, 268, 434 (a = 381), and 625 mμ (a = 414). (Other evidence will be cited to indicate that these two species are the same.)

The Decomposition of Peroxychromium(III) Species in Acidic Solution. Each green peroxychromium(III) species decomposes in acidic aqueous solution to produce oxygen, chromium(VI), and hexaaquochromium(III). During decomposition of the dimer, the spectrum changes as shown in Figure 3. Isosbestic points are observed at 387 and 326 mμ, indicating that the stoichiometry (*1.00 mole of* $Cr_2O_2^{4+}$ *gives 0.22 mole of* $HCrO_4^-$ *plus 0.34 mole of* O_2) holds throughout the decomposition. Using the known spectra of reactant and product chromium species, one would expect for this stoichiometry the isosbestic points to be at 383 and 326 mμ. One can express the net change in the decomposition in terms of a chemical equation

$$Cr_2O_2^{4+} + 1.12H^+ = 0.22HCrO_4^- + 1.78Cr^{3+} + 0.34O_2 + 0.45H_2O$$

Within experimental error, the recovery of chromium(VI) and hexaaquochromium(III) accounted for all of the chromium present initially as $Cr_2O_2^{4+}$.

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(10) M. Ardon and R. A. Plane, *J. Am. Chem. Soc.*, 81, 3197 (1959).
(11) L. S. Hegedus and A. Haim, *Inorg. Chem.*, 6, 664 (1967).

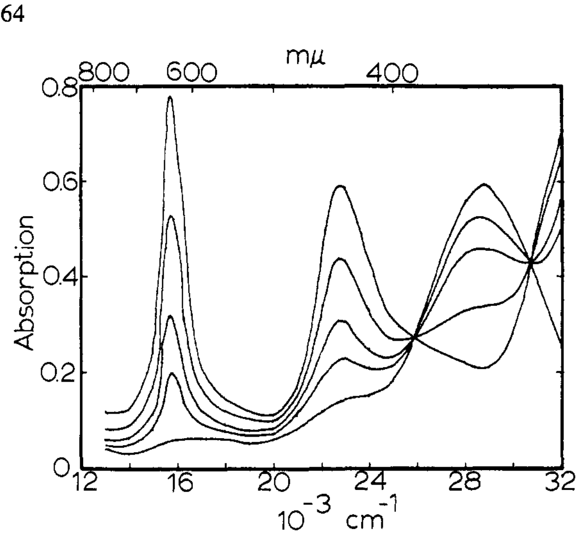

Figure 3. The spectrum of a solution of $Cr_2O_2^{4+}$ in 2 *M* $HClO_4$ as a function of time. $[Cr_2O_2^{4+}]_0 = 9.7 \times 10^{-4}$ *M*. The curves (from top to bottom at 634 mμ) are for times 0, 20, 40, 60, and 140 min, respectively. (In addition to the isosbestic points, support for constancy of stoichiometry during decomposition is given by values of $\Delta A_{350}/\Delta A_{634}$. Comparing adjacent curves, these values are −0.51, −0.58, −0.56, and −0.42.) Temperature 25.5°; 2-cm cell.

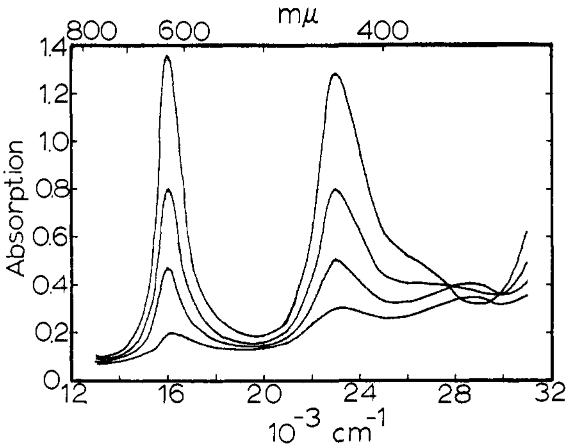

Figure 4. The spectrum of a solution of $Cr_3(O_2)_2^{5+}$ ($[Cr_3(O_2)_2^{5+}]_0 = 6.2 \times 10^{-4} M$) in 5 *M* $HClO_4$ at 25.5° as a function of time. The curves are (reading down at 625 mμ) for 0, 1.5, 3.0, and 9.5 hr (2-cm cell).

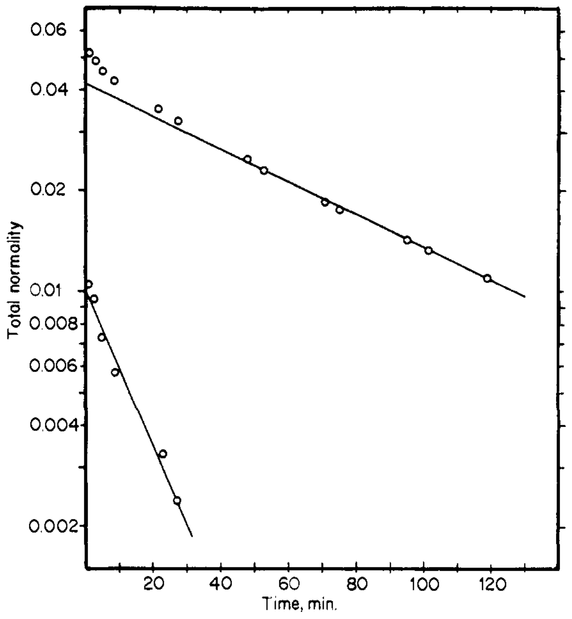

Figure 5. Oxidizing normality of a mixture of peroxychromium(III) species (logarithmic scale) *vs.* time. Medium, 2 *M* $HClO_4$; temperature 0°. (In this experiment, there was excess hydrogen peroxide present at zero time (2.6×10^{-3} *M*) and a low concentration of chromium(VI) (6×10^{-4} *M*) at 119 hr, the last point.) The two resolved first-order rate constants are 3.1×10^{-6} and 14.4×10^{-6} sec.$^{-1}$ Values obtained under these conditions in experiments using separated species (see Table II) are 3.35×10^{-6} and 15×10^{-6}, respectively. The upper set of points gives total normality *vs.* time, and the lower set is a plot of total normality *minus* extrapolated values from the straight line of the upper plot *vs.* time (*i.e.*, the normality due to shorter lived species *vs.* time).

The stoichiometry of decomposition of the trimer is not as simple as that of the dimeric species. For three experiments in 2 *M* perchloric acid at 0° with the initial concentrations of $Cr_3(O_2)_2^{5+}$ ranging from 0.007 to 0.013 *M*, in which there was present a slight excess of hydrogen peroxide, the stoichiometry of decomposition corresponded to 0.19 mole of hydrogen chromate ion formed per mole of $Cr_3(O_2)_2^{5+}$. In these experiments the concentrations of excess hydrogen peroxide (which decreases as chromium(VI) is produced) and trimer $Cr_3(O_2)_2^{5+}$ were determined as a function of time, and the data are consistent with the stoichiometry remaining essentially constant during the decomposition reaction. If the initial concentration of $Cr_3(O_2)_2^{5+}$ was very low, the stoichiometry changed from the value just reported, and there is spectral evidence that the stoichiometry varies during the course of a run. Figure 4 shows spectra as a function of time for a run at 25.5° in 5 *M* perchloric acid in which the initial concentration of $Cr_3(O_2)_2^{5+}$ was 9.3×10^{-4} *M*. Although an isosbestic point exists during initial stages of the reaction (at wavelengths which correspond to the production of 0.19 mole of hydrogen chromate ion per mole of $Cr_3(O_2)_2^{5+}$), this stoichiometry does not persist to the end of the experiment. At the lower concentrations, less than 0.19 mole of chromium(VI) is produced in the decomposition of 1 mole of $Cr_3(O_2)_2^{5+}$. Decomposition of trimer also produces some hydrolytic polymeric chromium(III) species. In two quantitative experiments, ~20% of the chromium present initially as $Cr_3(O_2)_2^{5+}$ was not recovered as hexaaquochromium(III) or chromium(VI). In one of these experiments the hydrolytic species were recovered partially from the ion-exchange resin by using barium ion as eluting agent.

Kinetics of the Decomposition Reactions. Data on the rate at which the oxidizing normality of an unprocessed reaction mixture decreases with time, combined with measured values of the concentration of chromium(VI) as a function of time (the latter quantities having been obtained by separation of chromium(VI) by an ion-exchange procedure), allow calculation of the oxidizing normality due to the green peroxychromium(III) species as a function of time. The results from such an experiment (given in Figure 5) show the presence of two oxidizing species. In the experiment shown in Figure 5, the decrease in oxidizing capacity with time at 0° is resolved into two independent first-order reactions with half-times of 13.3 and 62 hr.

The rates of decomposition of the dimer and the trimer have been measured after the species were purified by ion exchange. Figure 6 shows the results of experiments with each of the species. In these experiments the course of reaction was followed by spectral measurements at appropriate wavelengths. The first-order rate constants were calculated: $k = \Delta \ln (A - A_\infty)/\Delta t$, with A_∞ obtained at >8 half-times. A summary of the rate constants observed in the several kinetic experiments is given in Table II. There is substantial agreement between the rate constants obtained in the spectrophotometric runs starting with pure species and those resolved from the time dependence of the oxidizing normality of solutions containing both species. The dimer decomposes more rapidly than the trimer.

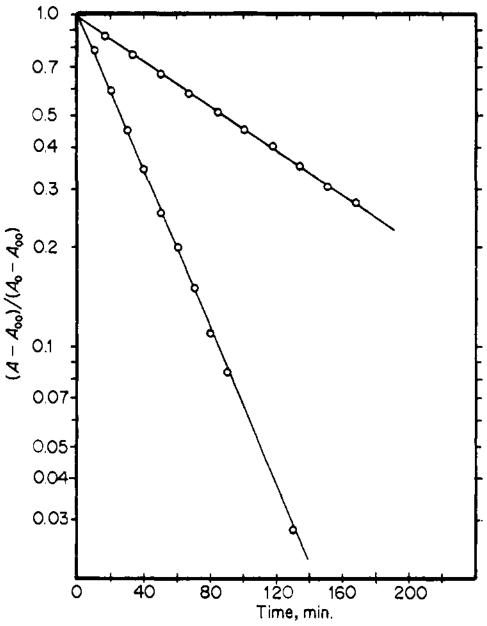

Figure 6. Extent of decomposition of peroxychromium(III) species (logarithmic scale) *vs.* time, temperature 25°. Upper curve, $Cr_3(O_2)_2^{5+}$, in 5 M $HClO_4$ ($[Cr_3(O_2)_2^{5+}]_0 = 9.3 \times 10^{-3}$ M). Data taken at 625 mμ. Lower curve, $Cr_2O_2^{4+}$ in 2 M $HClO_4$, ($[Cr_2O_2^{4+}]_0 = 9.7 \times 10^{-4}$ M). Data taken at 634 and 439 mμ. (With the exception of one point, the data at the two wavelengths agreed.)

Table II. First-Order Rate Coefficients for Decomposition of Peroxychromium(III) Species

	$Cr_2O_2^{4+}$ in 2.0 M $HClO_4$		
Temp, °C	$[Cr_2O_2^{4+}]_0$, M	Time followed	10^5k, sec^{-1}
0	9.2×10^{-4}	28 hr	1.5
25.5	9.7×10^{-4}	130 min	46.4[a]

		$Cr_3(O_2)_2^{5+}$		
Temp, °C	$[Cr_3(O_2)_2^{5+}]_0$, M	$[H^+]$, M	Time followed	10^5k, sec^{-1}
0	0.00050	5.0	240 hr	0.31
	0.0083	2.0	168 hr	0.33[b]
	0.0139	2.0	95 hr	0.34[b]
25.5	0.00045	1.0	230 min	10
	0.00093	5.0	167 min	13[a]
	0.00097	5.0	143 min	14
	0.00115	5.0	67 min	12
	0.00120	5.0	108 min	14[c]

[a] Run shown in Figure 5. [b] Solution also contained ~0.015 M H_2O_2; rate constant obtained from log (normality due to $Cr_3(O_2)_2^{5+}$) *vs.* time. The solutions were aged to allow decomposition of $Cr_2O_2^{4+}$ before measurement. [c] A_∞ determined after only 4.8 hr ($3.5t_{1/2}$).

The Reaction of the Longer Lived Peroxychromium(III) Species ($Cr_3(O_2)_2^{5+}$) with Oxidizing and Reducing Agents. In addition to the reactions of peroxychromium(III) species with reducing agents (iron(II) and iodide ion) used for analytical purposes, studies were made involving the longer lived species ($Cr_3(O_2)_2^{5+}$) with various oxidizing and reducing agents. These studies were made using aged reaction mixtures in which the dimer, $Cr_2O_2^{4+}$, had decomposed before addition of the oxidizing or reducing agent. The solutions contained, therefore, hexaaquochromium(III) ion and chromium(VI) in addition to trimer, $Cr_3(O_2)_2^{5+}$. After addition of the oxidizing or reducing agent, the solution was allowed to stand in the dark at room temperature for 24 hr or longer. The oxidizing normality of the solution was then determined by means of the iron(II)–cerium(IV) titrations. The normality of the added oxidizing agent was subtracted from the total normality to give the oxidizing normality of the chromium(VI) which was formed.

The reaction with cerium(IV) was studied initially with the expectation that cerium(IV) would oxidize the bound peroxide to oxygen. *This reaction does not occur!!* Rather, cerium(IV) at concentrations much lower than the concentration of the green species preserves some of the oxidizing capacity which would be lost by the decomposition reaction in the absence of cerium(IV). The preservation of oxidizing capacity cannot, therefore, be a simple stoichiometric reaction involving cerium(IV), and it seemed appropriate to investigate the effect of cerium(III). Cerium(III) was found also to preserve oxidizing capacity. The results of the experiments involving the two oxidation states of cerium are presented in Figure 7.

The other reagents studied were chromium(VI) and manganese(VII), which partially preserve the oxidizing capacity, and manganese(II), thallium(I), and thallium(III), which do not. Thallium(III), in fact, causes enhanced loss of oxidizing capacity.

Some observations were made of the time dependence of light absorption at 625 mμ (a maximum in the spectrum of $Cr_3(O_2)_2^{5+}$) of solutions of trimeric green species in the presence of cerium(III) and cerium(IV). In an experiment at 25.5° in 2 M perchloric acid with 9.3 × 10^{-4} M cerium(III) and an initial concentration of $Cr_3(O_2)_2^{5+}$ of 6.8 × 10^{-4} M, the spectral change followed for ~70% reaction was first order with a half-time of 1.4 hr, which isesse ntially the same as observed in the absence of cerium(III) (see Figure 6 and Table II). In the presence of cerium(IV), however, the rate was much greater, and it did not conform to first-order kinetics in an experiment (at 25.5° in 2 M perchloric

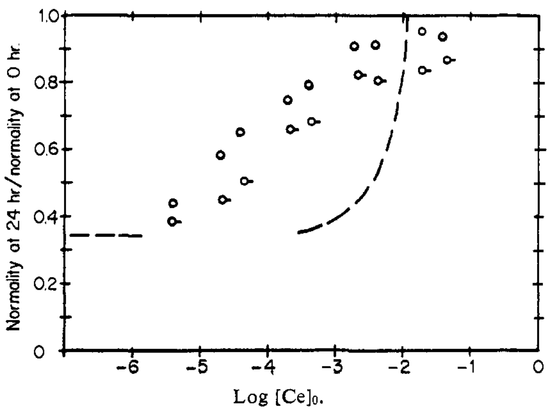

Figure 7. Oxidizing capacity preserved (normality at 24 hr/normality at zero time) as a function of stoichiometric concentration of added cerium. Upper set of points, ○, cerium(IV) added; lower set of points ○-, cerium(III) added. Medium 1.0 M $HClO_4$, 1.0 M H_2SO_4; initial concentration of $Cr_3(O_2)_2^{5+}$ = 6.2 × 10^{-3} M in cerium(IV) experiments; 4.6 × 10^{-3} M in cerium(III) experiments. The dashed line gives the expected preservation of oxidizing capacity if the mechanism was solely the reaction $2Ce^{IV} + Cr_3(O_2)_2^{5+} = 2HCrO_4^- + 2Ce^{3+}$ (see text), with the unreacted $Cr_3(O_2)_2^{5+}$ giving 0.345 as the fraction of oxidizing capacity preserved. This is the value observed at this initial concentration of $Cr_3(O_2)_2^{5+}$ in the absence of cerium.

acid) with initial concentrations 9.6 × 10^{-4} M cerium(IV) and 7.3 × 10^{-4} M $Cr_3(O_2)_2^{5+}$. The values for the time in minutes and the absorption (log I_0/I for 1-cm cell) at 625 mμ in this experiment were: 0, 0.838; 2, 0.392; 9, 0.132; 16, 0.076; 26, 0.044; 34, 0.036; 49, 0.030; and 103, 0.020.

Discussion

On the basis of ease of elution and oxidizing capacity, the compositions proposed for two different unstable green intermediates formed in the reaction of hydrogen peroxide and chromium(VI) in acidic solution are $Cr_2O_2^{4+}$, probably bridged $(H_2O)_5CrO_2Cr(OH_2)_5^{4+}$, and $Cr_3(O_2)_2^{5+}$, probably bridged $(H_2O)_5CrO_2Cr(OH_2)_4O_2$-$Cr(OH_2)_5^{5+}$. The latter composition is different than that suggested for the same species by Ardon and Bleicher.[5] On the basis of a measured oxidizing capacity very close to 1.5 units per chromium atom, they suggest the composition and structure $(H_2O)_5$-$CrO_2Cr(OH_2)_5^{5+}$. Their analyses were based upon the reaction with iodide, which was found in the present study to give higher normalities than obtained in the reaction with iron(II), or by disproportionation in alkaline solution, which was found in the present study to give spurious results unless the chromium(III) was removed before the spectrophotometric analysis for chromium(VI). It is possible, therefore, to explain the qualitative difference between the analytical results of the two studies (although the analytical data of the present study show appreciable scatter). An additional mild argument against the formulation involving fewer electrons than correspond to an oxidation state of 3+ for each chromium atom is the expected greater lability of such species. (This argument is not strong, however, since House, Hughes, and Garner[12] have found diperoxo species of chromium(IV) to be inert enough in aqueous ammoniacal solutions to allow spectral measurements.) Activation parameters for decomposition of the longer-lived species also tend to support its formulation as a species of chromium(III).

As already stated, the first-order rate constant for decomposition of the trimer, $Cr_3(O_2)_2^{5+}$, is in good agreement with the data presented by Ardon and Bleicher.[5] The data of both studies over a temperature range from 0 (the present study) to 36.5° (ref 5) are correlated with activation parameters, $\Delta H^{\ddagger}$ = 22.3 kcal mole^{-1} and $\Delta S^{\ddagger}$ = −2.3 cal mole^{-1} deg^{-1}, which are very similar in magnitude to values for the aquation of some chromium(III) species in which the chromium(III)–ligand bond is broken; *e.g.*, $\Delta H^{\ddagger}$ = 23.8 kcal mole^{-1} and $\Delta S^{\ddagger}$ = −3.5 cal mole^{-1} deg^{-1} for bromochromium(III) ion,[13] and $\Delta H^{\ddagger}$ = 23.0 kcal mole^{-1} and $\Delta S^{\ddagger}$ = −0.2 cal mole^{-1} deg^{-1} for iodochromium(III) ion.[14] This suggests, but does not prove, that the rate-determining step in the decomposition is the breaking of a chromium(III)–peroxide bond. The argument is strengthened by the fact that the enthalpy of activation for breaking of the oxygen–oxygen bond in peroxides is considerably higher (29–39 kcal mole^{-1} in various examples mentioned by Walling[15]).

Formulation of the two species as dimer and trimer is supported by the relative yields as a function of reactant concentrations (Table I). The yield of dimer relative to hexaaquochromium(III) ion increases as the chromium concentration increases, and the yield of trimer relative to dimer also increases with the same change in concentration conditions. It is interesting to note that in the experiment at the highest concentration of chromium(VI) a third *green* species was formed. Since it was less easily eluted than the trimer of charge 5+, it is reasonable to suggest that this species may be $Cr_4(O_2)_3^{6+}$, a tetramer with bridging peroxide units.

The more easily eluted species formulated as $Cr_2O_2^{4+}$ with 1.00 unit of oxidizing capacity per chromium atom exhibits stoichiometry in oxidation–reduction reactions exactly the same as chromium(IV). The proposed dimeric peroxychromium(III) formulation is more reasonable, however, in view of the concentration dependence of its yield relative to that of hexaaquochromium(III) ion. Although the temperature coefficient of the first-order rate constant for decomposition of this species is based on fewer data (only two temperatures, 0 and 25.5°), the derived activation parameters $\Delta H^{\ddagger}$ = 21.5 kcal mole^{-1} and $\Delta S^{\ddagger}$ = −2.3 cal mole^{-1} deg^{-1} suggest that the rate-determining step for this decomposition reaction is the same type of change as that in decomposition of the trimer, the breaking of a chromium(III)–ligand bond.

The mechanism of formation of the green peroxychromium(III) species is not clear. Although observation of the blue color of peroxychromium(VI) prior to formation of green species suggests that the latter species might be formed directly from peroxychromium(VI), the conclusion is not a rigorous one, and the work of others[16] suggests the formation of other less stable reac-

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[12] D. A. House, R. G. Hughes, and C. S. Garner, *Inorg. Chem.*, 6 1077 (1967).

[13] F. A. Guthrie and E. L. King, *ibid.*, 3, 916 (1964).

[14] T. W. Swaddle and E. L. King, *ibid.*, 4, 532 (1965).

[15] C. Walling, "Free Radicals in Solution," John Wiley and Sons, Inc., New York, N. Y., 1957, pp 469–511.

tion intermediates, which may be precursors of the species investigated in the present study. Orhanović and Wilkins[17] have studied the rate of decomposition of blue peroxychromium(VI) in acidic solution, a reaction which is first order in CrO_5 and second order in hydrogen ion, and they conclude that the green peroxychromium(III) species are not formed in decomposition of peroxychromium(VI) in dilute solution ($<10^{-4}$ M CrO_5). An intermediate species with shorter lifetime than either peroxychromium(III) species has been studied by Morrow and associates.[16] Whatever the mechanism of formation of the dimeric and trimeric peroxychromium(III) species, the observed stoichiometry (2.5–3.0 moles of hydrogen peroxide per mole of chromium(VI)) indicates that oxygen production occurs in addition to that required by the balanced equation(s) for the over-all reaction(s).

Since the rate of decomposition of each of the green peroxychromium(III) species is low on the time scale of a preparative experiment, neither of these species is a compulsory intermediate en route to production of hexaaquochromium(III) ion. If such were the case, the yield of peroxychromium(III) dimer and trimer would be much higher. A monomeric peroxychromium(III) species may be an intermediate on the pathway to production of hexaaquochromium(III) ion in the preparative experiments, however. (This species will be suggested also as a short-lived intermediate in the decomposition of dimeric peroxychromium(III) species.)

The failure in the present study to obtain dimeric $Cr_2O_2^{4+}$ in the oxygen oxidation of chromium(II) does not prove that this species is not an intermediate in the production of the hydrolytic dimer of chromium(III) (which is the predominant product when chromium(II) is in excess). Our data indicate only that $Cr_2O_2^{4+}$ is not produced under our experimental conditions. The reaction of chromium(II) and oxygen in 1:1 proportions would produce a species with a net oxidizing capacity equivalent to that of chromium(VI). Production of hydrogen chromate ion from such a species by reaction with solvent would be possible.

$$CrO_2^{2+} + 2H_2O \longrightarrow HCrO_4^- + 3H^+$$

If this reaction occurred with high efficiency, one would expect the final products to be those from the chromium(VI)–chromium(II) reaction, $\geqslant 50\%$ hexaaquochromium(III) ion and $\leqslant 50\%$ hydrolytic dimer, which are roughly the observations. If the species CrO_2^{2+} persisted long enough for reaction with chromium(II), the peroxychromium(III) dimer $Cr_2O_2^{4+}$ would be produced. In experiments in which oxygen is added to a solution of chromium(II) (the procedures of Ardon and Plane[10] and Kolaczkowski and Plane[8]), the much higher concentration of chromium(II) favors the formation of $Cr_2O_2^{4+}$ and also its subsequent reaction with chromium(II) to produce hydrolytic dimer of chromium(III). Presumably there are concentration conditions which would allow isolation of some dimeric peroxychromium(III) species ($Cr_2O_2^{4+}$) in the reaction of chromium(II) and oxygen, but they have not been found in the present study.

A question which arises in consideration of the decomposition reaction(s) is whether or not the shorter lived dimer is formed in decomposition of the longer lived trimer. A reaction scheme

$$Cr_3(O_2)_2^{5+} \xrightarrow{k_1} Cr_2O_2^{4+} \xrightarrow{k_2}$$

could give a linear variation of log $\{(A - A_\infty)/(A_0 - A_\infty)\}$ with time if measurements were started after the transient steady state had been established. In experiments performed with purified $Cr_3(O_2)_2^{5+}$, many data were taken at times short compared to the time required for the transient steady state to be established. Since the light absorption due to $Cr_2O_2^{4+}$ at the wavelength of this study (625 mμ) is appreciable (360 l. mole^{-1} cm^{-1}) compared to that of $Cr_3(O_2)_2$ (645 l. mole^{-1} cm^{-1}), the linear plot given in Figure 6 *is not consistent* with the production of $Cr_2O_2^{4+}$ in the decomposition of $Cr_3(O_2)_2^{5+}$.

The preservation of oxidizing capacity in the presence of an oxidizing agent or a reducing agent indicates that such reagents open pathways for conversion of the oxidizing capacity of bound peroxide to chromium (VI). Cerium (IV) can do this in the reaction

$$4H_2O + 2CeSO_4^{2+} + Cr_3(O_2)_2^{5+} = 2HCrO_4^- + 2Ce^{3+} + Cr^{3+} + 2HSO_4^- + 4H^+$$

but if this were the complete explanation, complete preservation of oxidizing capacity could be achieved only if the concentration of cerium(IV) were equal to or greater than two times the concentration of trimer. Data in Figure 7 show, however, that such a stoichiometric amount of cerium(IV) is not needed. This is explained satisfactorily if peroxychromium(III) species are capable of oxidizing cerium(III)

$$4H^+ + 4Ce^{3+} + 4HSO_4^- + Cr_3(O_2)_2^{5+} = 4CeSO_4^{2+} + 3Cr^{3+} + 4H_2O$$

With these two reactions occurring at rates which maintain constant concentrations of cerium(IV) and cerium(III), the net change occurring in the system is

$$3Cr_3(O_2)_2^{5+} + 4H_2O = 4HCrO_4^- + 5Cr^{3+} + 4H^+$$

and it would be appropriate to say that this net reaction is catalyzed by the cerium(III)–cerium(IV) couple. It cannot be asserted, however, that a steady state was established in the experiments given in Figure 7, but this does not alter the argument that some combination of the two reactions is responsible for preservation of oxidizing capacity.

Our limited study of the stoichiometry of the reaction of chromium(II) and chromium(VI) indicates that the mechanism proposed by Ardon and Plane[10] does not account completely for results in dilute solutions of the

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[16] J. I. Morrow, R. A. Pinkowitz, and J. Laufer, *Inorg. Chem.*, **5**, 934 (1966).

[17] M. Orhanović and R. G. Wilkins, *J. Am. Chem. Soc.*, **89**, 278 (1967).

reactants. The reaction proposed by Ardon and Plane for production of hydrolytic dimer

$$Cr^{IV} + Cr^{2+} + 2H_2O = Cr_2(OH)_2^{4+} + 2H^+$$

must be less important in our experiments as the process by which chromium(IV) is consumed compared to a reaction or sequence of reactions which produce hexaaquochromium(III) ion. A possible sequence is

$$Cr^{IV} + H_2O \rightleftharpoons Cr(OH_2)_6^{3+} + H^+ + OH$$

followed by

$$Cr^{2+} + OH + H^+ \longrightarrow Cr(OH_2)_6^{3+}$$

This mechanism would be more important at low concentrations of chromium. Production of hydroxyl radicals by chromium(IV) is undoubtedly an unfavorable reaction, but even at low concentrations hydroxyl radicals could probably compete effectively with chromium(IV) for chromium(II) ion. If this mechanism is responsible for the decreased yield of hydrolytic dimer, the yield should be a function of the concentration of hexaaquochromium(II) ion. Regrettably, no experiments were performed in which the concentration of hexaaquochromium(III) was varied systematically.

Although the decomposition of each of the peroxychromium(III) species follows first-order kinetics, the stoichiometry is not simple in either case. The activation energy for decomposition of each of the peroxychromium(III) species is consistent with the rate-determining step being the breaking of a chromium(III)–peroxide bond. The approximately constant stoichiometry in decomposition of dimer $Cr_2O_2^{4+}$ suggests that the branching must occur in competing processes which are the same order in species the concentrations of which change during the decomposition reaction. The competing processes might involve CrO_2H^{2+} (formed in the rate-determining step in decomposition of $Cr_2O_2^{4+}$).

$$2H_2O + CrO_2H^{2+} \longrightarrow H_2CrO_4^- + 3H^+$$

$$H^+ + CrO_2H^{2+} \longrightarrow Cr^{3+} + H_2O_2$$

The first of these reactions, conversion of the oxidizing capacity of bound peroxide to an increase of oxidation state for the metal ion, is analogous to a reaction in the iron(III)-catalyzed decomposition of hydrogen peroxide[18]

$$FeO_2H^{2+} \longrightarrow FeO^{3+} + OH^-$$

in which a species of iron(V) is produced. In the framework of the present discussion, it is this conversion of the monomeric chromium(III)–peroxide species to chromium(V) which is responsible for the failure to detect the monomeric species at appreciable concentrations in the present study. There are numerous possible reactions which consume chromium(V) and peroxide to produce the observed products, and the data at hand do not allow additional meaningful discussion regarding the mechanism of decomposition of dimer. The complicated processes occurring in the hydrogen peroxide–iron(III) system[19] may have analogs in the present system.

A feature of the decomposition of trimer which deserves additional discussion is the production (in low yield) of the hydrolytic dimer of chromium(III) ($Cr_2(OH)_2^{4+}$). As already suggested, the first step in the decomposition of $Cr_3(O_2)_2^{5+}$ appears to be production of Cr^{3+} and $Cr_2(O_2)_2^{2+}$. The latter species may undergo reaction producing hydrolytic dimer

$$2H^+ + CrO_2CrO_2^{2+} \longrightarrow Cr_2(OH)_2^{4+} + O_2$$

in which the bridging peroxide is reduced to form two bridging hydroxide ions and the peripheral peroxide is oxidized to oxygen. It may also produce monomeric peroxychromium(III)

$$2H^+ + CrO_2CrO_2^{2+} \longrightarrow 2CrO_2H^{2+}$$

the fate of which has already been discussed. The extent to which the species $Cr_2(O_2)_2^{2+}$ gives $Cr_2O_2^{4+}$ is low since the kinetic data are not consistent with trimer decomposing to give dimer.

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[18] This intermediate is shown as being protonated. The complex of iron(III) and hydrogen peroxide has charge 2+ (FeO_2H^{2+}) in the pH range 1–3 (M. G. Evans, P. George, and N. Uri, *Trans. Faraday Soc.*, **45**, 230 (1949)).

[19] M. L. Kremer, *ibid.*, **58**, 702 (1962).