

TABLE I  
RATES OF ACID HYDROLYSIS IN 0.1 M HNO<sub>3</sub> AT 25°

Complex	10 <sup>4</sup> k, sec. <sup>-1</sup>	E*, kcal.	ΔS*, cal./deg.
<i>trans</i> -[Co(en) <sub>2</sub> Br <sub>2</sub> ] <sup>+</sup>	1.40 <sup>a</sup>	26 <sup>a</sup>	+9 <sup>a</sup>
<i>trans</i> -[Cr(en) <sub>2</sub> Br <sub>2</sub> ] <sup>+</sup>	3.26	22.4	-1.38

<sup>a</sup> 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<sub>3</sub>, 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 <sup>4</sup> k, sec. <sup>-1</sup>
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.<sup>8</sup>

(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.

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## Oxygen Atom Transfer in the Oxidation of Aqueous Chromium(II) by Hydrogen Peroxide<sup>1</sup>

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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.

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

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).<sup>2,3</sup> 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<sub>2</sub>O<sup>18</sup> 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<sub>2</sub>O<sup>18</sup>, while hydrogen peroxide was of ordinary isotopic composition. Thus, peroxide oxygen was labeled relative to its H<sub>2</sub>O<sup>18</sup>-enriched solvent environment. Oxygen-18 exchange between water and hydrogen peroxide is a very slow process in acidic solutions.<sup>4</sup>

Reactant solutions containing chromous perchlorate and those containing hydrogen peroxide were separately enriched to the same known mole fraction of H<sub>2</sub>O<sup>18</sup> 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<sup>18</sup>O<sup>18</sup>/total CO<sub>2</sub> was determined on a mass spectrometer. This isotope ratio and the ratio for nonenriched CO<sub>2</sub> are combined with the known constant for the CO<sub>2</sub><sup>18</sup>-H<sub>2</sub>O<sup>18</sup> exchange equilibrium to obtain the mole fraction of H<sub>2</sub>O<sup>18</sup> in the original water sample.<sup>5</sup>

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<sub>2</sub>O<sup>18</sup>-enriched solvent for several months. The mole fraction of H<sub>2</sub>O<sup>18</sup>

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

(3) R. W. Kolaczowski and R. A. Plane, *Inorg. Chem.*, **3**, 322 (1964).

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

(5) R. A. Plane and H. Taube, *J. Phys. Chem.*, **56**, 33 (1952).

TABLE I  
 RESULTS OF ISOTOPE DILUTION EXPERIMENTS

Chromium soln.	Oxidizing soln.	$N_e^\infty \times 10^{8a}$	$N_e^{5/6} \times 10^{8b}$	$N_{obsd} \times 10^{8c}$
0.113 M Cr <sup>+3</sup>	None	10.13	...	9.72 (10.11)
0.0113 M Cr <sup>+3</sup>	None	10.13	...	9.75 (10.14)
0.304 M Cr <sup>+2</sup>	0.348 M Fe <sup>+3</sup>	9.69	...	9.26 (9.63)
0.157 M Cr <sup>+2</sup>	0.499 M Fe <sup>+3</sup>	10.15	...	9.77 (10.16)
0.157 M Cr <sup>+2</sup>	0.499 M Fe <sup>+3</sup>	10.15	...	9.79 (10.18)
0.276 M Cr <sup>+2</sup>	0.175 M H <sub>2</sub> O <sub>2</sub>	8.04	7.12	6.84 (7.11)
0.517 M Cr <sup>+2</sup>	1.18 M H <sub>2</sub> O <sub>2</sub>	9.05	7.93	7.60 (7.90)
0.517 M Cr <sup>+2</sup>	10.2 M H <sub>2</sub> O <sub>2</sub>	9.05	7.93	7.63 (7.93)
0.079 M Cr <sup>+2</sup>	0.93 M H <sub>2</sub> O <sub>2</sub>	9.65	8.43	8.09 (8.41)
0.079 M Cr <sup>+2</sup>	0.93 M H <sub>2</sub> O <sub>2</sub>	9.65	8.43	8.14 (8.46)
0.506 M Cr <sup>+2</sup>	1.18 M H <sub>2</sub> O <sub>2</sub>	10.36	9.03	8.71 (9.06)
0.506 M Cr <sup>+2</sup>	1.18 M H <sub>2</sub> O <sub>2</sub>	10.36	9.03	8.69 (9.04)
0.86 M Cr <sup>+2</sup>	1.02 M H <sub>2</sub> O <sub>2</sub>	9.86	8.62	8.29 (8.62)
0.86 M Cr <sup>+2</sup>	1.02 M H <sub>2</sub> O <sub>2</sub>	9.86	8.62	8.33 (8.66)
0.506 M Cr <sup>+2</sup>	0.82 M H <sub>2</sub> O <sub>2</sub>	6.79	6.07	5.86 (6.09)
0.506 M Cr <sup>+2</sup>	0.82 M H <sub>2</sub> O <sub>2</sub>	6.79	6.07	5.85 (6.08)

<sup>a</sup> The H<sub>2</sub>O<sup>18</sup> mole fraction calculated for random distribution of all isotopes. <sup>b</sup> The H<sub>2</sub>O<sup>18</sup> mole fraction expected if one-sixth of the bound water derives from hydrogen peroxide. <sup>c</sup> The observed H<sub>2</sub>O<sup>18</sup> mole fraction in the bound water (values in parentheses have been corrected for a 4% decrease in *N* introduced by the procedure).

calculated for random distribution of isotopes is the  $N_e^\infty$  value. The observed H<sub>2</sub>O<sup>18</sup> mole fraction,  $N_{obsd}$ , is the value for water removed from hexaaquochromium(III) fluoride which was precipitated from the chromium(III) solutions. The observed values are about 4% lower than the values calculated for random distribution of H<sub>2</sub>O<sup>18</sup>. The slightly low values are not attributable to incomplete exchange, as the results were independent of time. Isotopic fractionation during partial pyrolysis may occur to some extent; however agreement between  $N_e^\infty$  and  $N_{obsd}$  is better than 1% when there is no H<sub>2</sub>O<sup>18</sup> enrichment. Small amounts of ordinary water may become trapped in the crystals of hexaaquochromium fluoride during precipitation. Whatever the cause, the approximately 4% lowering of *N* introduced by the procedure was quite reproducible for the levels of H<sub>2</sub>O<sup>18</sup> enrichment used.

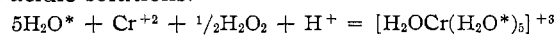
In the next three experiments, solutions containing chromium(II) and solutions containing ferric ion (which is labile to substitution) were separately enriched to the same H<sub>2</sub>O<sup>18</sup> mole fraction, which is the value shown under  $N_e^\infty$  for each experiment. The solutions were then mixed to convert labile chromous ion to nonlabile hexaaquochromium(III). Water removed from hexaaquochromium(III) fluoride in this case again gave H<sub>2</sub>O<sup>18</sup> mole fractions which were about 4% below the calculated values. With hydrogen peroxide as oxidizing agent, however, there was a large discrepancy (about 16%) between  $N_e^\infty$  and  $N_{obsd}$ , although each oxidizing and reducing solution was first separately enriched in H<sub>2</sub>O<sup>18</sup> to the value  $N_e^\infty$  before the reactions were carried out. The only nonenriched source of oxygen-16 was hydrogen peroxide itself.

In Table I, the quantity  $N_e^{5/6}$  represents the anticipated mole fraction for water bound to chromium(III) ion if calculated under the assumption that five water molecules per chromium derive from solvent water at

the mole fraction  $N_e^\infty$ , while the sixth water derives from hydrogen peroxide. The values of  $N_{obsd}$  are all about 4% below the  $N_e^{5/6}$  values. For the two calibration experiments, the agreement between  $N_{obsd}$  and  $N_e^\infty$  is  $96.1 \pm 0.1\%$ . For the experiments with iron as oxidizing agent,  $N_{obsd}$  is  $96.1 \pm 0.4\%$  of  $N_e^\infty$ . The agreement between  $N_{obsd}$  and  $N_e^{5/6}$  for the peroxide experiments, is  $96.3 \pm 0.3\%$  for eleven runs, which is just the value one would expect in view of the blanks, run first.

### Discussion

The results in Table I indicate that one oxygen atom per hexaaquochromium(III) comes directly from the hydrogen peroxide which reacts with chromium(II) in the acidic solutions.



This reaction is very fast and is apparently complete within several milliseconds when carried out in our rapid flow apparatus.

Also, competing processes are involved, as is evidenced by the simultaneous formation of violet hexaaquochromium(III) and varying amounts of a green form of chromium(III) in the reaction. Peroxide decomposition is a possible side reaction; oxygen is known to react rapidly with chromium(II), and the product is  $[(H_2O)_4CrOH]_2^{+4}$ , a green dimer.<sup>3</sup>

Some inferences regarding electron transfer may be drawn from the present atom transfer result. Cahill and Taube<sup>6</sup> have studied the chromium(II)-peroxide reaction. They interpret their results in terms of a two-electron transfer process, which involves rupture of the peroxide O-O bond in the initial step and yields chromium(IV). The latter is subsequently reduced to chromium(III). Indirect experimental evidence and the electronic structure of chromium(IV) indicate that it should be highly labile toward substitution.<sup>7</sup> Thus, chromium(IV) would be expected to exchange water molecules in its hydration sphere with those in the solvent quite rapidly. After reduction of the labile chromium(IV) to nonlabile chromium(III), very little of the peroxide oxygen would be found attached to the chromium(III). The present result is that precisely one oxygen atom per hexaaquochromium(III) comes from hydrogen peroxide.

This result seems to mean that there is an initial "one-electron" oxidation to produce CrOH<sup>+2</sup> and an OH radical. The hydroxyl radical may then react with the excess peroxide or with chromium(II) to form a second chromium(III) ion containing in its hydration shell one oxygen atom derived from hydrogen peroxide. One question is this in view of the possibility of rapid oxygen atom exchange between water and hydroxyl radical<sup>8</sup> before reaction with chromium(II). However, the other processes may be faster. Hydrogen peroxide is known to be an efficient "scavenger" for OH radicals.<sup>9</sup>

(6) A. E. Cahill and H. Taube, *J. Am. Chem. Soc.*, **74**, 2312 (1952).

(7) A. E. Ogard and H. Taube, *J. Phys. Chem.*, **62**, 357 (1958).

(8) O. L. Forchheimer and H. Taube, *J. Am. Chem. Soc.*, **76**, 2099 (1954).

(9) M. Anbar, S. Guttman, and G. Stein, *J. Chem. Phys.*, **34**, 703 (1961).

Any oxygen liberated in the solution will combine rapidly with chromium(II) to give the dimeric species. It should be noted, however, that the observed dimer

may well come about as the result of a competing "two-electron" oxidation to chromium(IV) and its subsequent reaction with chromium(II).

## Correspondence

### Evidence for Unidentate Acetylacetonate Ligand in $\text{Na}_2\text{Pt}(\text{acac})_2\text{Cl}_2 \cdot 5\text{H}_2\text{O}$

Sir:

The crystal structure of  $\text{KPt}(\text{acac})_2\text{Cl}$ <sup>1</sup> shows the coordination sphere around platinum to consist of the chloride ion, a bidentate acetylacetonate ion, and a unidentate acetylacetonate ion bonded through the  $\gamma$ -carbon. This unusual structure has prompted us to report our results on a similar compound,<sup>2</sup>  $\text{Na}_2\text{Pt}(\text{acac})_2\text{Cl}_2 \cdot 5\text{H}_2\text{O}$ .

Our original interest was in finding a six-coordinate platinum(II) complex. Such compounds are rare,<sup>3</sup> but would be of interest thermodynamically and spectrochemically. The stoichiometry of this salt suggests that it could contain such an ion, since the acetylacetonate ion generally serves as a bidentate ligand. However, on the bases of spectral and chemical evidence, we believe that this compound contains two unidentate acetylacetonate ligands in both solid and aqueous phases.

The infrared spectra of transition metal acetylacetonates exhibit one, two, or three bands in the region between 1520 and 1600  $\text{cm}^{-1}$  which are associated with the  $\text{C}=\text{O}$  ( $\nu_1$ ) and  $\text{C}=\text{C}$  ( $\nu_2$ ) stretching vibrations. In addition a band at about 780  $\text{cm}^{-1}$  ( $\nu_3$ ) is presumably associated with the C-H out-of-plane bending vibration.<sup>4-6</sup> Pertinent frequencies of several of these acetylacetonates are compared with those of  $\text{KPt}(\text{acac})_2\text{Cl}$  and  $\text{Na}_2\text{Pt}(\text{acac})_2\text{Cl}_2 \cdot 5\text{H}_2\text{O}$  (Table I).

Since  $\nu_1$  for  $\text{Na}_2\text{Pt}(\text{acac})_2\text{Cl}_2 \cdot 5\text{H}_2\text{O}$  occurs at higher energy than those of the symmetrically coordinated ions, especially  $\text{Pt}(\text{acac})_2$ , we conclude that the bonding is significantly different. We note that, while the split components of  $\nu_1$  are of somewhat lower energy than those of  $\text{KPt}(\text{acac})_2\text{Cl}$ , it is still in the correct region for a carbonyl group in conjugation with

TABLE I  
FREQUENCIES IN WAVE NUMBERS,  $\text{CM}^{-1}$

Compound	$\nu_1$	$\nu_2$	$\nu_3$
$\text{Al}(\text{acac})_3$	1600	1535	774
$\text{Cu}(\text{acac})_2$	1580	1530	780
$\text{Pt}(\text{acac})_2$	1565	1535	777
$\text{KPt}(\text{acac})_2\text{Cl}$	1695	Not reported	Not reported
$\text{Na}_2\text{Pt}(\text{acac})_2\text{Cl}_2 \cdot 5\text{H}_2\text{O}$	1660	1550	
	1640	1540	

a  $\text{C}=\text{C}$  linkage.<sup>7</sup> Significantly, there is no evidence of a band in the region of 780  $\text{cm}^{-1}$ , although  $\text{Pt}(\text{acac})_2$  shows a sharp and intense band in this region.

Further evidence for unidentate acetylacetonate ion is provided by the positive reaction of this compound with 2,4-dinitrophenylhydrazine, hydroxylamine, and  $\text{NaHSO}_3$ , reagents which are specific for a free carbonyl group. The analytical results for the dinitrophenylhydrazine derivatives show conclusively that two carbonyl groups are available for reaction. *Anal. Calcd.* for  $\text{Na}_2[\text{PtCl}_2\text{C}_{22}\text{H}_{22}\text{O}_{10}\text{N}_8]$ : C, 30.3; H, 2.53; Cl, 8.17; N, 12.9; Pt, 22.4. *Found*: C, 30.8; H, 2.62; Cl, 8.20; N, 13.1; Pt, 22.0. Similar reactions with  $\text{Al}(\text{acac})_3$  were attempted in alcohol-water mixtures with negative results.

Our results do not exclude an axially elongated octahedron possessing two thermodynamically and kinetically weak Pt-O bonds. Such a structure might account for the spectral and chemical evidence, but steric requirements of the acetylacetonate ion seem to preclude this possibility. Our results do not enable us to distinguish unequivocally between two  $\gamma$ -carbon-bonded acetylacetonate ligands, or two oxygen-bonded acetylacetonate ligands, or a combination of both. It is interesting to note that the reaction of phenylhydrazine with free acetylacetonate produces N-phenylpyrazine. This fact alone, however, does not allow us to reach a firm conclusion with the present knowledge of template reactions.

(7) L. J. Bellamy, "The Infrared Spectra of Complex Molecules," Methuen and Co., London, p. 136.

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(2) A. Werner, *Ber.*, **34**, 2584 (1901).

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(4) K. Nakamoto and A. E. Martell, *J. Chem. Phys.*, **32**, 588 (1960).

(5) K. Nakamoto, P. J. McCarthy, A. Ruby, and A. E. Martell, *J. Am. Chem. Soc.*, **83**, 1088 (1961).

(6) K. Nakamoto, P. J. McCarthy, and A. E. Martell, *ibid.*, **83**, 1272 (1961).