

**Table III.** Data Used in the Calculation of the Arrhenius Activation Energy, the Enthalpy of Activation, and the Entropy of Activation for the Second Step in the Formation of Violet Peroxychromate

temp, °C	$10^{-4}k_2$ , $M^{-2} s^{-1}$	$K_B^a$ , $M^{-1}$	$10^{-4}k_2$ , $M^{-1} s^{-1}$	$\ln(k_2/T)$
15	1.08	0.18	6.00	5.339
25	1.59	0.16	9.94	5.809
35	1.89	0.14	13.5	6.082

<sup>a</sup> Evaluated for an ionic strength of 1.0 (see ref 10). The values for  $K_B$  at 15 and 35 °C are calculated by using the integrated van't Hoff equation with  $\Delta H^\circ = -2.1$  kcal.

the last step the formation of blue and violet peroxychromates proceed via a common mechanism.

It is possible to extract from our data an activation energy, enthalpy, and entropy for the rate-determining step of the violet reaction. Using the data presented in Table III, one obtains the Arrhenius rate expression for step 2

$$k_2 = 10^{10.2 \pm 0.8} \exp [(-7200 \pm 1000 \text{ cal})/RT]$$

A plot of  $\ln(k_2/T)$  vs.  $1/T$  gives an activation enthalpy and entropy of  $6.6 \pm 1.0$  kcal and  $-14 \pm 4$  cal/K, respectively, for the slow step. A parallel analysis by ourselves of Wilkins' data<sup>4</sup> for the blue reaction gives  $\Delta H^\ddagger = 6.0$  kcal and  $\Delta S^\ddagger = -15$  cal/K, substantiating the view that the blue and violet reactions have common rate-determining steps.<sup>12</sup>

**Acknowledgment.** We wish to thank Professors Scaife and Weick of the Union College Chemistry Department for many helpful discussions throughout the course of this project. Also, the loan of a dual-channel thermocouple with digital display from the Silicone Products Business Division of the General Electric Co., Waterford, NY, is greatly appreciated.

**Registry No.**  $\text{HCrO}_4^-$ , 15596-54-0;  $\text{H}_2\text{O}_2$ , 7722-84-1;  $\text{HCrO}_6^-$ , 40330-52-7.

(12) It should be noted that Orhanovic and Wilkins<sup>5</sup> have reported an enthalpy and entropy of activation for  $\text{CrO}_5 \cdot \text{H}_2\text{O}$  formation of 3900 cal and  $-26$  cal/K, respectively. These numbers are not obtained from  $k_2$  but rather appear to be calculated with the third-order rate constant  $k$ . As such, their values for  $\Delta H^\ddagger$  and  $\Delta S^\ddagger$  would not be comparable to our own.

Contribution from the Chemistry Division, Argonne National Laboratory, Argonne, Illinois 60439, and the Chemistry Departments, Nuclear Research Centre Negev, and Ben-Gurion University of the Negev, Beer-Sheva, Israel

## Homolytic Decomposition of Tertiary Organochromium(III) Complexes and Evidence for Their Decomposition via Reactions with Aliphatic Free Radicals. A Pulse Radiolysis Study<sup>1</sup>

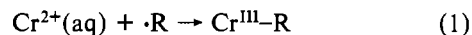
WILLIAM A. MULAC,<sup>2a</sup> HAIM COHEN,<sup>2b</sup> and DAN MEYERSTEIN\*<sup>2</sup>

Received December 8, 1981

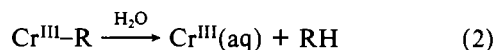
The rates of homolytic decomposition of  $\text{Cr}-\text{C}(\text{CH}_3)_2\text{OH}^{2+}$ ,  $\text{Cr}-\text{C}(\text{CH}_3)_2\text{CO}_2\text{H}^{2+}$ , and  $\text{Cr}-\text{C}(\text{CH}_3)_2\text{CN}^{2+}$  are  $0.15 \text{ s}^{-1}$ ,  $4 \text{ s}^{-1}$ , and  $10^4 < k < 10^6 \text{ s}^{-1}$ , respectively. The reaction of some aliphatic free radicals,  $\cdot\text{R}$  with  $\text{Cr}^{\text{III}}-\text{R}$  complexes is very fast,  $k_3 \geq 10^8 \text{ M}^{-1} \text{ s}^{-1}$ . The rate of reaction of  $\text{Cr}^{2+}(\text{aq})$  with  $\text{H}_2\text{O}_2$  is  $k_{16} = (3.7 \pm 0.7) \times 10^4 \text{ M}^{-1} \text{ s}^{-1}$  in good accord with the literature value. These results are discussed in detail.

### Introduction

Saturated aliphatic free radicals are known to react with  $\text{Cr}^{2+}(\text{aq})$  to form organochromium(III) complexes:<sup>3,4</sup>



The rates of reaction 1 are high,  $(1 \times 10^7) - (1 \times 10^9) \text{ M}^{-1} \text{ s}^{-1}$ , for all the free radicals studied.<sup>4</sup> Some of the aliphatic residues rearrange due to the influence of the trivalent chromium.<sup>4,5</sup> All the aliphatic organochromium(III) complexes studied<sup>3d,4</sup> were shown to decompose heterolytically in aqueous solutions via



Recently Espenson and co-workers have shown that in the presence of efficient scavengers for  $\text{Cr}^{2+}(\text{aq})$  and/or  $\cdot\text{R}$  ( $\alpha$ -hydroxyalkyl)- and ( $\alpha$ -alkoxyalkyl)chromium(III) complexes decompose homolytically.<sup>5</sup> The results indicate that the rate of homolysis increases with the introduction of steric hindrance to the chromium-carbon bond.<sup>5</sup> In another study Espenson<sup>6</sup> reported the formation of  $\text{Cr}-\text{CH}_2\text{CN}^{2+}$ ,  $\text{Cr}-\text{CH}_2\text{CH}_2\text{CN}^{2+}$ , and  $\text{Cr}-\text{CH}_2\text{CH}(\text{CH}_3)\text{CN}^{2+}$ , which are all relatively stable in aqueous solutions. However, the formation of  $\text{Cr}-\text{CH}(\text{CH}_3)\text{CN}^{2+}$  and  $\text{Cr}-\text{C}(\text{CH}_3)_2\text{CN}^{2+}$  was not observed though

the corresponding free radicals are known to be formed. It was suggested that the latter observation is due to a high rate of homolysis of the latter two complexes.<sup>6</sup>

We decided to try to measure the rates of homolysis of  $\text{Cr}-\text{CH}(\text{CH}_3)\text{CN}^{2+}$  and  $\text{Cr}-\text{C}(\text{CH}_3)_2\text{CN}^{2+}$  using the pulse radiolytic technique, which enables the observation of short-lived intermediates.<sup>7,8</sup> For comparison we decided to measure also the rates of homolysis of  $\text{Cr}-\text{C}(\text{CH}_3)_2\text{CO}_2^+$  and  $\text{Cr}-\text{C}(\text{CH}_3)_2\text{OH}^{2+}$  (the latter was measured in order to check the technique). We were unable to measure the rate of homolysis of  $\text{Cr}-\text{CH}(\text{CH}_3)\text{CN}^{2+}$  but report here the rates of homolysis of the other complexes, which increase along the series  $\text{Cr}-$

\* To whom correspondence should be addressed at Ben-Gurion University of the Negev.

- (1) Work performed in part under the auspices of the Office of Basic Energy Sciences, Division of Chemical Sciences, of the U.S. Department of Energy.
- (2) (a) Argonne National Laboratory. (b) Nuclear Research Centre Negev. (c) Ben-Gurion University of the Negev.
- (3) (a) Anet, F. A. L.; Leblanc, E. *J. Am. Chem. Soc.* **1957**, *79*, 2649. (b) Kochi, J. K.; Davis, D. D. *Ibid.* **1964**, *86*, 5264. (c) Coombes R. G.; Johnson, M. D.; Winterton, J. *J. Chem. Soc. A* **1965**, 7029. (d) Schmidt, W.; Swinehart, J. H.; Taube, H. *J. Am. Chem. Soc.* **1971**, *93*, 1117. (e) Bakač, A.; Espenson, J. H. *J. Am. Chem. Soc.* **1980**, *102*, 2488.
- (4) Cohen, H.; Meyerstein, D. *Inorg. Chem.* **1974**, *13*, 2434.
- (5) Kirker, G. W.; Bakač, A.; Espenson, J. H., personal communication.
- (6) Funke, L. A.; Espenson, J. H. *Inorg. Chem.* **1981**, *20*, 897.
- (7) Matheson, M.; Dorfman, L. M. "Pulse Radiolysis"; MIT Press: Cambridge, MA, 1969.
- (8) Meyerstein, D. *Acc. Chem. Res.* **1978**, *11*, 43.

Table I. Rates of Reactions between Cr<sup>2+</sup>(aq) and H<sub>2</sub>O<sub>2</sub>, k<sub>16</sub>

organic solute	10 <sup>-4</sup> k <sub>16</sub> , M <sup>-1</sup> s <sup>-1</sup>	
	excess Cr <sup>2+</sup> (aq)	excess H <sub>2</sub> O <sub>2</sub> <sup>a</sup>
CH <sub>3</sub> CN	4.0 ± 0.4	3.2 ± 0.4
CH <sub>3</sub> CH <sub>2</sub> CN	4.5 ± 0.8	7.5 ± 0.8
CH(CH <sub>3</sub> ) <sub>2</sub> CN	3.0 ± 0.4	6.3 ± 1.0
CH(CH <sub>3</sub> ) <sub>2</sub> CO <sub>2</sub> H		8.0 ± 2.0

<sup>a</sup> Rates calculated with the assumption that two chromous ions are consumed in the reaction (see text).

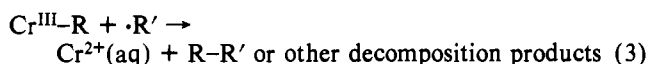
Table II. Homolytic Rates of Decomposition of Tertiary Chromium-Carbon σ Bonds

Cr complex	k <sub>-1</sub> , s <sup>-1</sup>	Cr complex	k <sub>-1</sub> , s <sup>-1</sup>
Cr-CH(CH <sub>3</sub> ) <sub>2</sub> <sup>2+</sup>	2.4 × 10 <sup>-4</sup> <sup>a</sup>	Cr-C(CH <sub>3</sub> ) <sub>2</sub> CO <sub>2</sub> H <sup>2+</sup>	4 <sup>c</sup>
Cr-C(CH <sub>3</sub> ) <sub>2</sub> OH <sup>2+</sup>	0.13 <sup>b</sup>	Cr-C(CH <sub>3</sub> ) <sub>2</sub> CN <sup>2+</sup>	10 <sup>4</sup> ≤ k <sub>-1</sub> ≤ 10 <sup>6</sup> <sup>c</sup>

<sup>a</sup> Reference 27 in ref 5. <sup>b</sup> Reference 5. <sup>c</sup> This work.

CH(CH<sub>3</sub>)<sub>2</sub><sup>2+</sup>, Cr-C(CH<sub>3</sub>)<sub>2</sub>OH<sup>2+</sup>, Cr-C(CH<sub>3</sub>)<sub>2</sub>CO<sub>2</sub><sup>+</sup>, and Cr-C(CH<sub>3</sub>)<sub>2</sub>CN<sup>2+</sup>.

The results obtained also corroborate the earlier reported rate of reaction of Cr<sup>2+</sup>(aq) with H<sub>2</sub>O<sub>2</sub><sup>9</sup> and indicate that aliphatic free radicals react with organochromium(III) complexes via



The rates of reaction 3 are relatively high, and the products of reactions were not isolated.<sup>10</sup>

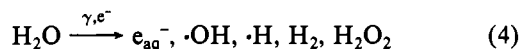
### Experimental Section

**Materials.** Chromous perchlorate solutions were prepared by dissolving high purity grade chromium powder in dilute HClO<sub>4</sub> under continuous bubbling of argon. All other chemicals were of analytical grade and were used without further treatment. All water used was triple-distilled.

**Irradiation.** Short electron pulses from the linear accelerators at Argonne National Laboratory and the Hebrew University of Jerusalem were used. The dose per pulse was in the range (1.0 × 10<sup>3</sup>)–(1.3 × 10<sup>4</sup>) rd/pulse. The kinetics were followed spectrophotometrically. The experimental setups as well as the techniques used for evaluating the results have been described earlier in detail.<sup>12,13</sup> All experiments were carried out at room temperature, 22 ± 2 °C; no effort to maintain a constant ionic strength was made.

### Results and Discussion

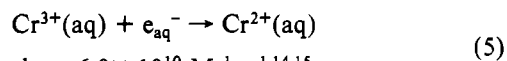
The radiolysis of water can be summed up by the equation<sup>7</sup>



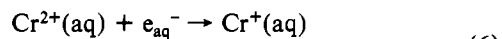
The primary products are formed with yields of G<sub>e<sub>aq</sub><sup>-</sup></sub> = G<sub>OH</sub> = 2.65, G<sub>H</sub> = 0.60, G<sub>H<sub>2</sub></sub> = 0.45, and G<sub>H<sub>2</sub>O<sub>2</sub></sub> = 0.75.<sup>7</sup> (G is given in number of molecules formed per 100 eV absorbed in the solution.) The radical yields are somewhat larger and the molecular yields somewhat lower in the presence of high concentrations of free-radical scavengers.<sup>7</sup>

In acidic solutions containing Cr<sup>2+</sup>(aq), Cr<sup>3+</sup>(aq), H<sub>2</sub>O<sub>2</sub>, and organic solutes of the general formula CH<sub>3</sub>CHRX (where R

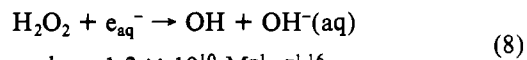
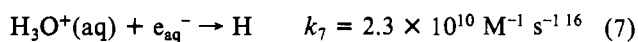
≡ CH<sub>3</sub> or H and X ≡ OH, CN, or CO<sub>2</sub>H) reactions 1–3 and reactions 5–17 have to be considered. The rates of reaction



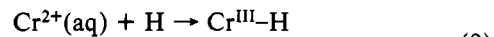
$$k_5 = 6.0 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1,14,15}$$



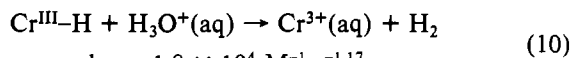
$$k_6 = 4.2 \times 10^{10} \text{ M}^{-1} \text{ s}^{-14}$$



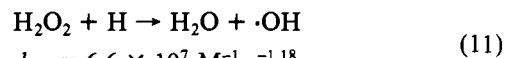
$$k_8 = 1.2 \times 10^{10} \text{ M}^{-1} \text{ s}^{-16}$$



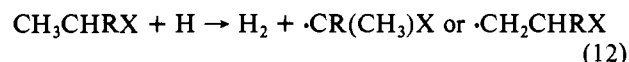
$$k_9 = 1.5 \times 10^9 \text{ M}^{-1} \text{ s}^{-17}$$



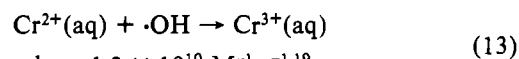
$$k_{10} = 1.8 \times 10^4 \text{ M}^{-1} \text{ s}^{-17}$$



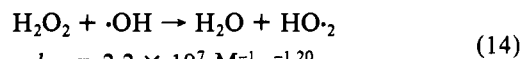
$$k_{11} = 6.6 \times 10^7 \text{ M}^{-1} \text{ s}^{-18}$$



(the yield of ·CR(CH<sub>3</sub>)X is considerably larger than that of ·CH<sub>2</sub>CHRX)



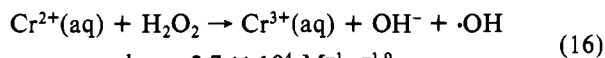
$$k_{13} = 1.2 \times 10^{10} \text{ M}^{-1} \text{ s}^{-19}$$



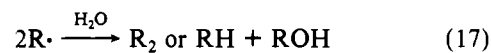
$$k_{14} = 2.2 \times 10^7 \text{ M}^{-1} \text{ s}^{-20}$$



(the yield of ·CR(CH<sub>3</sub>)X is considerably higher than that of ·CH<sub>2</sub>CHRX)



$$k_{15} = 2.7 \times 10^4 \text{ M}^{-1} \text{ s}^{-19}$$



(where ·R = ·CR(CH<sub>3</sub>)X or ·CH<sub>2</sub>CHRX; when a more accurate definition of ·R will be required, we will use the notation ·R<sub>1</sub> = ·CR(CH<sub>3</sub>)X and ·R<sub>2</sub> = ·CH<sub>2</sub>CHRX)

of e<sub>aq</sub><sup>-</sup> with CH<sub>3</sub>CHRX,<sup>16</sup> of H and ·OH with Cr<sup>3+</sup>(aq),<sup>18,20</sup> and of the free radicals with H<sub>2</sub> are too small to affect the kinetics studied. Under our experimental conditions also reactions 11 and 13 have little effect if any on the kinetics observed. The rates of reactions of the free radicals ·R with H<sub>2</sub>O<sub>2</sub> are assumed to be low and probably do not affect the kinetics studied. (Of the free radicals used in this study only the rate of reaction of ·C(CH<sub>3</sub>)<sub>2</sub>OH with H<sub>2</sub>O<sub>2</sub>, k = 5 × 10<sup>5</sup> M<sup>-1</sup> s<sup>-1</sup>, has been reported.<sup>21</sup> The other radicals used are known to be weaker reducing agents, and therefore their rates

(14) Anbar, M.; Hart, E. J. *J. Phys. Chem.* **1965**, *69*, 973.

(15) The rate reported is for Cr(H<sub>2</sub>O)<sub>6</sub>OH<sup>2+</sup>; that for Cr(H<sub>2</sub>O)<sub>6</sub><sup>3+</sup> is expected to be somewhat higher.

(16) Anbar, M.; Bambenek, M.; Ross, A. B. *Natl. Stand. Ref. Data Ser. (U.S., Natl. Bur. Stand.)* **1973**, NSRDS-NBS 43.

(17) Cohen, H.; Meyerstein, D. *J. Chem. Soc., Dalton Trans.* **1974**, 1974.

(18) Anbar, M.; Farhatziz; Ross, A. B. *Natl. Stand. Ref. Data Ser. (U.S., Natl. Bur. Stand.)* **1975**, NSRDS-NBS 51.

(19) Samuni, A.; Meisel, D.; Czapski, G. *J. Chem. Soc., Dalton Trans.* **1972**, 1275.

(20) Farhatziz; Ross, A. B. *Natl. Stand. Ref. Data Ser. (U.S., Natl. Bur. Stand.)* **1977**, NSRDS-NBS 59.

(21) Burchill, C. E.; Jones, P. W. *Can. J. Chem.* **1971**, *49*, 4005.

(9) Czapski, G.; Samuni, A.; Meisel, D. *J. Phys. Chem.* **1971**, *75*, 3271.

(10) The observation that pinacol is formed via Cr-C(CH<sub>3</sub>)<sub>2</sub>OH<sup>2+</sup> + ·C(CH<sub>3</sub>)<sub>2</sub>OH → Cr<sup>2+</sup> + (CH<sub>3</sub>)<sub>2</sub>C(OH)C(OH)(CH<sub>3</sub>)<sub>2</sub><sup>11</sup> indicates that at least in this system R-R' is the product of reaction 3 as acetone and 2-propanol are formed in the reaction between two ·C(CH<sub>3</sub>)<sub>2</sub>OH free radicals.

(11) Espenson, J. H., private communication.

(12) (a) Cohen, H.; Meyerstein, D. *J. Am. Chem. Soc.* **1972**, *94*, 6944. (b) Ilan, Y. Ph.D. Thesis, Hebrew University of Jerusalem, 1977.

(13) Gordon, S.; Mulac, W. A.; Schmidt, K. H.; Syoblom, R. K.; Sullivan, J. S. *Inorg. Chem.* **1978**, *17*, 294.

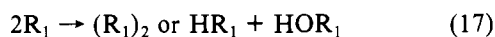
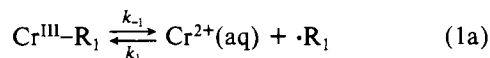
of reaction with  $\text{H}_2\text{O}_2$  are probably even slower.)

Two types of experiments were carried out for each of the organic solutes studied.

A. Solutions containing 0.1–0.5 M of the organic solute, RH, and  $(2-10) \times 10^{-4}$  M  $\text{Cr}^{2+}(\text{aq})$  at pH 1.0 and 2.0 were irradiated. Under these conditions all the  $\cdot\text{OH}$  radicals react via reaction 15 to form the free radicals  $\cdot\text{R}$ , and all the  $e_{\text{aq}}^-$  are transformed into  $\cdot\text{H}$  atoms via reaction 7. The fate of the  $\cdot\text{H}$  atoms depends on the relative rates of reactions 9 and 12 for the organic solute used. These reactions will be followed by the formation of  $\text{Cr}^{\text{III}}-\text{R}$ , reaction 1. We hoped to follow now the decomposition of  $\text{Cr}^{\text{III}}-\text{R}$ ; however, the results indicated that two other reactions complicated the kinetics observed. For all the organic solutes studied, with the exception of 2-propanol, reaction 9 competes considerably with reaction 12, and therefore reaction 10 is observed. As the rate of reaction 10 is known, it does not add an unknown step into the mechanism but complicates the detailed analysis of the changes in optical densities observed. In all cases studied, reaction 16 between the  $\text{H}_2\text{O}_2$  formed by the pulse, eq 4, and  $\text{Cr}^{2+}(\text{aq})$  occurs. The  $\cdot\text{OH}$  radicals formed react via reaction 15 followed by reaction 1 to form an additional amount of  $\text{Cr}^{\text{III}}-\text{R}$ . As reaction 16 is the rate-determining step in this sequence, the results are expected to verify the known value of  $k_{16}$ , which was measured by the stopped-flow technique under conditions that allowed measurements only with low accuracy.<sup>9</sup>

B. Solutions containing  $1 \times 10^{-2}$  M  $\text{Cr}^{3+}(\text{aq})$  and 0.1–0.5 M of the organic solute at pH 2.65 with  $0-5 \times 10^{-3}$  M  $\text{H}_2\text{O}_2$  were irradiated. Under these conditions most of the hydrated electrons reduce  $\text{Cr}^{3+}(\text{aq})$ , producing  $\text{Cr}^{2+}(\text{aq})$ , reaction 5, and only some disappear via reactions 7 or 8. Thus the  $\text{Cr}^{2+}(\text{aq})$  formed reacts with  $\cdot\text{R}$ , formed by reaction 15, to form  $\text{Cr}^{\text{III}}-\text{R}$ . The yield of  $\cdot\text{H}$  atoms in this system is small, and indeed reaction 10 was not observed under these conditions. The yield of  $\text{Cr}^{2+}(\text{aq})$  is somewhat smaller than that of  $\cdot\text{R}$ , but as  $k_1$  is considerably lower than  $k_{17}$ ,<sup>22</sup> some  $\text{Cr}^{2+}(\text{aq})$  remains in the solutions after all the  $\cdot\text{R}$  radicals reacted. When  $\text{H}_2\text{O}_2$  is added to the solution, this excess of  $\text{Cr}^{2+}(\text{aq})$  will react via the reaction sequence (16), (15), and (1). Again reaction 16 is the rate-determining step, but as two chromous ions are consumed in this sequence, the rate constant calculated from the pseudo-first-order formation of  $\text{Cr}^{\text{III}}-\text{R}$  corresponds to  $2k_{16}$ .

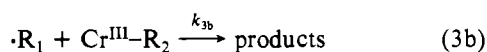
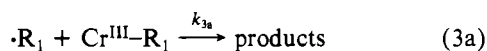
If  $\text{Cr}^{\text{III}}-\text{R}_1$  decomposes homolytically, the following reactions have to be considered:



If these are all the reactions contributing to the decomposition, then in the presence of excess  $\text{Cr}^{2+}(\text{aq})$

$$-\frac{d[\text{Cr}^{\text{III}}-\text{R}_1]}{dt} = k_{17} \frac{k_{-1}^2}{k_1^2} \frac{[\text{Cr}^{\text{III}}-\text{R}]^2}{[\text{Cr}^{2+}]^2} \quad (18)$$

If, however, reaction 3 is fast, then also reactions



have to be taken into account. Assuming the steady-state assumption for  $\cdot\text{R}_1$  and neglecting reaction 17, as  $[\text{Cr}^{\text{III}}-\text{R}] \gg [\cdot\text{R}_1]$ , one obtains

$$-\frac{d[\text{Cr}^{\text{III}}-\text{R}_1]}{dt} = \frac{2k_{-1}k_{3a}[\text{Cr}^{\text{III}}-\text{R}_1]^2 + k_{-1}k_{3b}[\text{Cr}^{\text{III}}-\text{R}_1][\text{Cr}^{\text{III}}-\text{R}_2]}{k_1[\text{Cr}^{2+}(\text{aq})] + k_{3a}[\text{Cr}^{\text{III}}-\text{R}_1] + k_{3b}[\text{Cr}^{\text{III}}-\text{R}_2]} \quad (19)$$

In the presence of excess  $\text{H}_2\text{O}_2$  the concentration of  $\text{Cr}^{2+}(\text{aq})$  is low, due to reaction 16, and the rate of decomposition of  $\text{Cr}^{\text{III}}-\text{R}_1$  will approach  $2k_{-1}[\text{Cr}^{\text{III}}-\text{R}_1]$ .

In the following sections the results obtained for the different organic solutes are discussed.

**2-Propanol.** When solutions containing excess  $\text{Cr}^{2+}(\text{aq})$  were irradiated, the lifetime of  $\text{Cr}-\text{C}(\text{CH}_3)_2\text{OH}^{2+}$  exceeded 1 min, even when low  $[\text{Cr}^{2+}(\text{aq})]$ , i.e.,  $1 \times 10^{-4}$  M was used. When solutions containing  $3.5 \times 10^{-3}$  M  $\text{Cr}(\text{ClO}_4)_3$ , 0.1 M  $\text{CH}(\text{CH}_3)_2\text{OH}$ , and  $(3-10) \times 10^{-2}$  M  $\text{H}_2\text{O}_2$  at pH 3.3 were irradiated, the lifetime of the transient was considerably shorter, obeying a first-order rate law independent of  $[\text{H}_2\text{O}_2]$ , with  $k_{-1}(\text{Cr}-\text{C}(\text{CH}_3)_2\text{OH}^{2+}) = 0.15 \pm 0.05 \text{ s}^{-1}$  in very good agreement with the results of Espeson et al.<sup>5,6</sup> Surprisingly enough similar results were obtained when no  $\text{H}_2\text{O}_2$  was added to the solutions; pulses producing ca.  $1.5 \times 10^{-5}$  M  $\text{Cr}^{2+}$  and ca.  $2.0 \times 10^{-5}$  M  $\cdot\text{C}(\text{CH}_3)_2\text{OH}$  were used. The kinetics observed under these conditions obeyed a first-order rate law with  $k = 0.020 \pm 0.005 \text{ s}^{-1}$ . The first-order rate law indicates that the decomposition reactions obey the rate law (19) with  $k_{-1}[\text{Cr}^{2+}(\text{aq})] \leq k_3[\text{Cr}-\text{C}(\text{CH}_3)_2\text{OH}^{2+}]$  and not the rate law (18).

The latter observation seems to be the first one which indicates that reaction 3 has to be considered in organochromium-containing systems.<sup>24</sup> Similar reactions were observed for other systems containing  $\sigma$  carbon-metal bonds in aqueous solutions.<sup>25</sup>

**Acetonitrile.** When solutions containing  $(2-10) \times 10^{-4}$  M  $\text{Cr}^{2+}$  and 0.5 M  $\text{CH}_3\text{CN}$  in the pH range 1.0–2.0 are irradiated, three consecutive reactions are observed. After these reactions are over, a product with the spectrum of  $\text{Cr}-\text{CH}_2\text{CN}^{2+}$  remains in the solution. The first reaction observed is the formation of  $\text{Cr}-\text{H}^{2+}$  (see below) and  $\text{Cr}-\text{CH}_2\text{CN}^{2+}$ . As ca. two-thirds of the absorption formed in this step, as measured at 290 nm, is due to  $\text{Cr}-\text{H}^{2+}$ , the rate observed corresponds to that of reaction 9. The results suggest, however, that  $k_1(\cdot\text{CH}_2\text{CN})$  is not considerably smaller than  $k_9$  as the two processes were not separated in time. The second process observed causes a decrease of ca. two-thirds in the absorption at 290 nm and obeys a pseudo-first-order rate law, the rate being also first order in  $[\text{H}_3\text{O}^+]$ ,  $k = (1.3 \pm 0.3) \times 10^4 \text{ M}^{-1} \text{ s}^{-1}$ , in reasonable agreement with  $k_{10}$ . We attribute therefore this process to reaction 10. The third process observed causes a slight increase of the absorbance and obeys a pseudo-first-order rate law, being also first order in  $[\text{Cr}^{2+}(\text{aq})]$ ; we attribute this process to reaction 16 and obtain  $k_{16} = (4.0 \pm 0.4) \times 10^4 \text{ M}^{-1} \text{ s}^{-1}$ . The same three processes were also observed in solutions containing  $1.0 \times 10^{-2}$  M  $\text{Cr}^{3+}$  and 0.5 M  $\text{CH}_3\text{CN}$  at pH 2.65 with  $(1-5) \times 10^{-3}$  M  $\text{H}_2\text{O}_2$ . From this system we obtain  $k_{16} = (3.2 \pm 0.4) \times 10^4 \text{ M}^{-1} \text{ s}^{-1}$ . We observed no reactions due to the radical  $\text{CH}_3\text{C}(\text{OH})=\text{N}\cdot$ <sup>6</sup>

**Propionitrile.** The results with this organic solute, 0.2 M, are similar to those discussed above for acetonitrile. However, the absorption at 290 nm of  $\text{Cr}-\text{CH}_2\text{CH}_2\text{CN}^{2+}$  and/or  $\text{Cr}-\text{CH}(\text{CH}_3)\text{CN}^{2+}$  relative to that of  $\text{Cr}-\text{H}^{2+}$  is much higher. Thus we were able to determine  $k_1$  in this system,  $k_1(\text{Cr}^{2+} + \cdot\text{CH}_2\text{CH}_2\text{CN}/\cdot\text{CH}(\text{CH}_3)\text{CN}) = (2.3 \pm 0.3) \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$ . It should be noted that this is not a pure rate constant as clearly two radicals contribute to the reaction observed. From this

(22) The specific rates of reaction 1 are reported below, and  $k_{17} = (1-3) \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$  for most noncharged saturated aliphatic radicals.<sup>23</sup>

(23) See, for example: Neta, P.; Simic, M.; Hayon, E. *J. Phys. Chem.* **1969**, *73*, 4207.

(24) Professor Espenson let us know that his group has also results pointing out that this reaction occurs; e.g., see ref 10.

(25) (a) Kelm, M.; Lilie, J.; Henglein, A.; Janata, E. *J. Phys. Chem.* **1974**, *78*, 882. (b) Kelm, M.; Lilie, J.; Henglein, A. *J. Chem. Soc., Faraday Trans. 1* **1975**, *71*, 1132.

system we obtain  $k_{10} = (1.4 \pm 0.3) \times 10^4 \text{ M}^{-1} \text{ s}^{-1}$  and  $k_{16} = (7.5 \pm 0.8) \times 10^4 \text{ M}^{-1} \text{ s}^{-1}$  from solutions with excess  $\text{H}_2\text{O}_2$  and  $k_{16} = (4.5 \pm 0.8) \times 10^4 \text{ M}^{-1} \text{ s}^{-1}$  from solutions with excess  $\text{Cr}^{2+}$ . The reasons for the large discrepancy between  $k_{16}$  values as obtained from the two techniques will be discussed below.

Under no conditions were we able to observe the kinetics of decomposition of  $\text{Cr}-\text{CH}(\text{CH}_3)\text{CN}^{2+}$ ,<sup>6</sup> which we were looking for. The reason for this is not clear. It might be due to the fact that the reaction has a rate similar to one of the other processes observed and/or that the yield and absorption coefficient of this compound are relatively small in the region studied.

**Isobutyronitrile.** When solutions containing 0.1 M  $\text{CH}(\text{C}-\text{H}_3)_2$  and  $(2-10) \times 10^{-4} \text{ M Cr}^{2+}$  at  $1.0 \leq \text{pH} \leq 2.0$  are irradiated, several processes are observed. The first reaction observed, which results in the formation of a transient with a spectrum typical of a chromium-carbon bond, obeys a pseudo-first-order rate law, the rate being proportional to  $[\text{Cr}^{2+}(\text{aq})]$ . From the results we calculate  $k_1[\text{Cr}^{2+}(\text{aq}) + \cdot\text{C}(\text{CH}_3)_2\text{CN}/\cdot\text{CH}_2\text{CH}(\text{CH}_3)\text{CN}] = 1.9 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$ . As for the propionitrile system this rate is not a true rate constant as we clearly observe two parallel reactions that are not separated in time.

The following reaction observed causes a decrease of over 50% in the absorption due to the transient but only minor changes in its spectrum. At pH 1.0 the reaction is better described as a second-order process with  $k/[(\Delta\epsilon)] = 5 \times 10^4$  and  $1.25 \times 10^5$  for  $[\text{Cr}^{2+}(\text{aq})] = 1 \times 10^{-3} \text{ M}$  and  $5 \times 10^{-4} \text{ M}$ , respectively (first-order rate law plots give  $k \approx 2.1 \times 10^3$  and  $2.8 \times 10^3 \text{ s}^{-1}$  for the same solutions). At pH 2.0 however the decomposition reaction is split into two consecutive processes. The first one obeys a second-order rate law with rates identical with those quoted above; however, the first-order best approximation gives now  $k \approx 8 \times 10^3 \text{ s}^{-1}$ . The second one obeys a first-order rate law with  $k = (1.4 \pm 0.3) \times 10^2 \text{ s}^{-1}$ , which suggests that the reaction observed is reaction 10, which has a rate of  $1.8 \times 10^3 \text{ s}^{-1}$  at pH 1.0<sup>17</sup> and is therefore not separated in time from the other process at this pH. We attribute the first process observed at pH 2.0 to the homolytic decomposition of  $\text{Cr}-\text{C}(\text{CH}_3)_2\text{CN}^{2+}$ . To calculate  $k_{-1}$  for this system, one can use eq 18 assuming  $k_{17} = 2 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$  and  $\epsilon_{290}(\text{Cr}-\text{R}) \approx 1000 \text{ M}^{-1} \text{ cm}^{-1}$ ,<sup>26</sup> which results in  $k_{-1} \approx 5 \times 10^7 \text{ s}^{-1}$ . However, if  $k_1/k_{-1} \approx 4$ , then nearly no  $\text{Cr}-\text{R}_1^{2+}$  would be formed under our experimental conditions. Furthermore the dependence of  $k$  on  $\text{Cr}^{2+}(\text{aq})$  is smaller than predicted. We used therefore eq 19 under conditions where  $k_1[\text{Cr}^{2+}(\text{aq})]$  is the major contributing factor in the denominator and assumed that  $k_3 = k_{3a} = k_{3b}$ . With these assumptions one obtains  $k_{-1}k_3 \approx 2 \times 10^{13}$ ; as  $k_3 \leq 2 \times 10^9$ , the diffusion-controlled limit for such reactions, clearly  $k_{-1} > 10^4 \text{ s}^{-1}$ . As we observe the formation of  $\text{Cr}-\text{C}(\text{CH}_3)_2\text{CN}^{2+}$ ,  $\text{Cr}-\text{R}_1^{2+}$ , in solutions containing  $5 \times 10^{-4} \text{ M Cr}^{2+}(\text{aq})$  clearly  $[\text{R}_1]/[\text{Cr}-\text{R}_1] \leq 10$ ; therefore,  $k_{-1} < 10^6 \text{ s}^{-1}$ . Thus we conclude that for this system  $10^4 < k_{-1} < 10^6 \text{ s}^{-1}$ .

After the decomposition of  $\text{Cr}-\text{H}^{2+}$  and  $\text{Cr}-\text{R}_1^{2+}$  is over, we observe the formation of  $\text{Cr}-\text{R}_2^{2+}$  due to reactions 16, 15, and 1. We calculate  $k_{16} = (3.0 \pm 0.4) \times 10^4 \text{ M}^{-1} \text{ s}^{-1}$  from this system. In solutions containing  $\text{Cr}^{3+}(\text{aq})$  and  $\text{H}_2\text{O}_2$  at pH 2.65 the homolytic decomposition is too fast to be observed and the only reaction observed, after the formation of  $\text{Cr}-\text{R}_2^{2+}$  via reaction 1, is due to reaction 16. The results here give  $k_{16} = (6.3 \pm 1.0) \times 10^4 \text{ M}^{-1} \text{ s}^{-1}$ .

**Isobutyric Acid.** When solutions containing  $(2-10) \times 10^{-4} \text{ M Cr}^{2+}(\text{aq})$  and 0.1 M  $\text{CH}(\text{CH}_3)_2\text{CO}_2\text{H}$  at pH 1.0 and 2.0 are irradiated, several processes are observed. The product

of the first reaction observed has a spectrum typical to a chromium-carbon complex. The reaction obeys a pseudo-first-order rate law from the results, indicating  $k_1[\text{Cr}^{2+}(\text{aq}) + \cdot\text{C}(\text{CH}_3)_2\text{COOH}/\cdot\text{CH}_2\text{CH}(\text{CH}_3)\text{CO}_2\text{H}] = (1.15 \pm 0.1) \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$ ; again these two reactions are not separated in time. This reaction is followed by a second process, which causes a slight decrease in the absorption due to the transients formed. The rate of this process, which obeys a pseudo-first-order rate law, is pH dependent and is attributed to reaction 10. From the results we calculate  $k_{10} = (1.9 \pm 0.4) \times 10^4 \text{ M}^{-1} \text{ s}^{-1}$ .

Following this reaction a further process causing a decrease of over 50% in the absorption due to the transients is observed. This process is attributed to the homolytic decomposition of  $\text{Cr}-\text{C}(\text{CH}_3)_2\text{COH}^{2+}$ . The kinetics do not fit well either a first-order rate law,  $k \approx 2.5 \text{ s}^{-1}$ , or a second-order rate law,  $k/\epsilon \approx 40 \text{ s}^{-1}$ . The rate seems to be nearly independent of  $[\text{Cr}^{2+}(\text{aq})]$ . These results suggest that eq 19 describes best the results and that in this case the term  $k_1[\text{Cr}^{2+}(\text{aq})]$  is not the major term in the denominator. Again, as the relative yields of  $\cdot\text{C}(\text{CH}_3)_2\text{CO}_2\text{H}$  and  $\cdot\text{CH}_2\text{CH}(\text{CH}_3)\text{CO}_2\text{H}$  and the molar absorption coefficients of the transients are unknown,  $k_{-1}$  can only be estimated from these results,  $k_{-1} \approx 10 \text{ s}^{-1}$ . (The formation of  $\text{Cr}-\text{R}^{2+}$ , due to reaction 16, was not observed under these conditions as it overlaps partially in time with the homolytic decomposition; this might also affect  $k_{-1}$  slightly.)

When solutions containing  $1 \times 10^{-2} \text{ M Cr}^{3+}(\text{aq})$ , 0.1 M  $\text{CH}(\text{CH}_3)_2\text{CO}_2\text{H}$ , and  $0-5 \times 10^{-3} \text{ M H}_2\text{O}_2$  at pH 2.65 were irradiated, the results are simpler. The first process observed after the formation of  $\text{Cr}-\text{R}^{2+}$  is reaction 16, for which we calculate  $k_{16} = (8 \pm 2) \times 10^4 \text{ M}^{-1} \text{ s}^{-1}$ . This reaction is followed by the homolytic decomposition of  $\text{Cr}-\text{C}(\text{CH}_3)_2\text{CO}_2\text{H}^{2+}$ , which under these conditions obeys a first-order rate law with  $k_{-1} = 4 \pm 2 \text{ s}^{-1}$ .

**Rate of Reaction 16.** In Table I are summed up the results obtained in this study for  $k_{16}$ . It is evident that for all the organic solutes used, with the exception of  $\text{CH}_3\text{CN}$ ,  $k_{16}$  obtained from experiments with excess  $\text{H}_2\text{O}_2$  is significantly larger than that obtained from experiments with excess  $\text{Cr}^{2+}(\text{aq})$ . The discrepancy is considerably larger than the experimental error and seems to be due to the effect of reaction 3 on the sequence of reactions 16, 15, and 1. The measurement of  $k_{16}$  in this study is based on the assumption that  $d[\text{Cr}-\text{R}]/dt = -d[\text{Cr}^{2+}]/2dt$ , when excess  $\text{H}_2\text{O}_2$  is present. When, however,  $k_3[\text{Cr}-\text{R}]$  attains a value of the same order of magnitude as  $k_1[\text{Cr}^{2+}]$ , this assumption is no longer correct. This clearly happens earlier when excess  $\text{H}_2\text{O}_2$  is used and  $[\text{Cr}^{2+}(\text{aq})]$  is low. When reaction 3 starts to compete with reaction 1, the apparent rate of reaction 16 increases as the maximal concentration of  $\text{Cr}-\text{R}^{2+}$  is formed faster. These results are in accord with the conclusion, derived from the measurements of  $k_{-1}$  above, that  $k_3 \geq 1 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$  for most of the systems studied. The results indicate that  $k_3$  for  $\cdot\text{CH}_2\text{CN} + \text{Cr}-\text{CH}_2\text{CN}^{2+}$  has a lower rate constant.

Thus we believe that  $\overline{k_{16}} = (3.7 \pm 0.7) \times 10^4 \text{ M}^{-1} \text{ s}^{-1}$ , obtained from the experiments with excess  $\text{Cr}^{2+}(\text{aq})$  and the  $\cdot\text{CH}_2\text{CN}$  system, is a better estimate for  $k_{16}$ . However, a smaller contribution of reaction 3 under these conditions cannot be ruled out and  $k_{16}$  might have even a somewhat lower value in agreement with  $k_{16} = 2.7 \times 10^4 \text{ M}^{-1} \text{ s}^{-1}$ .<sup>9</sup>

**Rate of Homolytic Decomposition of Tertiary Chromium-Carbon  $\sigma$  Bonds.** In Table II we summed up the reported rates for the homolytic decomposition of tertiary chromium-carbon bonds. The results clearly point out that the rate of homolytic decomposition of chromium(III)-carbon  $\sigma$  bonds depends not only on steric factors. It seems that the major other factor affecting the rate is the resonance stabilization of the free radical,  $\cdot\text{R}_1$ . This conclusion is in agreement with the relatively high rate of homolytic decomposition of the primary chro-

(26) As the relative yields of  $\cdot\text{CH}_2\text{CH}(\text{CH}_3)\text{CN}$  and  $\cdot\text{C}(\text{CH}_3)_2\text{CN}$  are not known, we obtain only an approximate average molar absorption coefficient for the two complexes with chromium-carbon bonds.

mium-carbon bond in  $\text{Cr-CH}_2\text{C}_6\text{H}_5^{2+27}$  and the very low rate of homolysis of  $\text{Cr-CH}(\text{CF}_3)\text{OH}^{2+}$ .<sup>5</sup>

**Acknowledgment.** We are thankful to Professor J. H. Espenson for fruitful discussions and for preprints describing unpublished results and to Professor G. Closs for encouragement and discussion throughout this work. This study was

(27) Nohr, R. S.; Espenson, J. H. *J. Am. Chem. Soc.* **1975**, *97*, 3392.

supported in part by the Petroleum Research Fund, administered by the American Chemical Society, by the United States Israel Binational Science Foundation (BSF), Jerusalem, Israel, and by the Israel Commission for Basic Research.

**Registry No.**  $\text{Cr-CH}(\text{CH}_3)_2^{2+}$ , 60764-48-9;  $\text{Cr-C}(\text{CH}_3)_2\text{OH}^{2+}$ , 32108-93-3;  $\text{Cr-C}(\text{CH}_3)_2\text{CO}_2\text{H}^{2+}$ , 82494-81-3;  $\text{Cr-C}(\text{CH}_3)_2\text{CN}^{2+}$ , 82494-82-4;  $\text{Cr-CH}_2\text{CN}^{2+}$ , 76068-68-3;  $\text{Cr-CH}_2\text{CH}_2\text{CN}^{2+}$ , 76068-69-4;  $\text{Cr-CH}(\text{CH}_3)\text{CN}^{2+}$ , 82494-83-5;  $\text{Cr}^{2+}(\text{aq})$ , 20574-26-9;  $\text{H}_2\text{O}_2$ , 7722-84-1.

Contribution from the Department of Chemistry,  
North-Eastern Hill University, Shillong 793003, India

## Alkali-Metal and Ammonium Triperoxyfluorovanadates(V), $\text{A}_2[\text{V}(\text{O}_2)_3\text{F}]$

MIHIR K. CHAUDHURI\* and SOUMITRA K. GHOSH

Received March 1, 1982

Blue alkali-metal and ammonium triperoxyfluorovanadates(V),  $\text{A}_2[\text{V}(\text{O}_2)_3\text{F}]$  (A =  $\text{NH}_4$ , Na, and K) have been synthesized by reacting  $\text{V}_2\text{O}_5$  with fluorides AF and hydrogen peroxide in a highly alkaline medium. The compounds have been characterized by elemental analyses, magnetic susceptibility measurements, and IR spectroscopic studies. The compounds do not permit molar conductance measurements. The IR spectra of the compounds suggest the presence of triangularly bonded peroxy ligands. The complex species  $[\text{V}(\text{O}_2)_3\text{F}]^{2-}$  may be a seven-coordinated monomer or it may have a polymeric structure through a weak V-F-V bridging. The basicity of peroxy ligands increases with the increase in the number of peroxy groups coordinated to the vanadium(V) center.

There has been a good deal of current interest in the study of peroxyvanadium(V) chemistry.<sup>1-6</sup> It appears from the recent literature that studies of the kinetic behavior of peroxyvanadium(V) engage the attention of most of the research groups,<sup>2-6</sup> though information on the synthesis and structural assessment of peroxyvanadium(V) is rather scanty, probably owing to the uncertain nature of peroxyvanadium(V) in solutions of varying pH. We have reported recently a short study on the synthesis and structural assessment of alkali-metal and ammonium oxydiperoyfluorovanadates(V),  $\text{A}_2[\text{VO}(\text{O}_2)_2\text{F}]$ . The compounds  $\text{A}_2[\text{VO}(\text{O}_2)_2\text{F}]$  were synthesized by performing the reactions over a limited range of concentration of alkaline medium.<sup>7</sup> We have now extended this work to an alkaline medium concentration region higher than that of the previously examined one, thus enabling us to synthesize a series of novel compounds, alkali-metal and ammonium triperoxyfluorovanadates(V),  $\text{A}_2[\text{V}(\text{O}_2)_3\text{F}]$  (A =  $\text{NH}_4$ , Na, and K), and to make some reasonable conclusions about the formation of various peroxy compounds of fluorovanadium(V). We have also investigated the IR spectra of these solid compounds in order to obtain a set of internally consistent data regarding the effect on the basicity of peroxy ligands by the increase in the number of peroxy groups coordinated to fluorovanadium(V).

### Experimental Section

All chemicals were of reagent grade. Infrared spectra were recorded on a Perkin-Elmer Model 125 spectrophotometer separately in KBr and in Nujol media. Experiments on molar conductance measurements were made by using a Philips PR 9500 conductivity bridge. Magnetic

susceptibility measurements were made by the Gouy method using  $\text{Hg}[\text{Co}(\text{NCS})_4]$  as the calibrant.

**Synthesis of Alkali-Metal and Ammonium Triperoxyfluorovanadates(V),  $\text{A}_2[\text{V}(\text{O}_2)_3\text{F}]$  (A =  $\text{NH}_4$ , Na, and K).** As the methods of syntheses of the ammonium, sodium, and potassium triperoxyfluorovanadates(V) are similar, only a representative method is described.

Pure  $\text{V}_2\text{O}_5$  and dry fluoride AF (A =  $\text{NH}_4$ , Na, or K) were taken with maintenance of the molar ratio of  $\text{V}_2\text{O}_5$  and AF at 1:2 and mixed thoroughly by powdering together in an agate mortar. The finely mixed powder was dissolved in 6% hydrogen peroxide, with use of 60.0 mL of hydrogen peroxide/g of  $\text{V}_2\text{O}_5$ , by stirring the solution magnetically. After dissolution was complete, the solution became transparent red. The solution was filtered to remove any undissolved impurity. To the filtrate was slowly added with continuous stirring an excess of hydroxide AOH (A =  $\text{NH}_4$ , Na, or K), with maintenance of the molar ratio of  $\text{V}_2\text{O}_5$  and AOH at 1:12. While the stipulated amount of ammonium hydroxide was added in the form of its 25% solution, sodium and potassium hydroxides were added in their solid form. The color of the solution changed from red to yellow and ultimately to blue with the progress of addition of the alkaline medium. After the addition of alkali-metal or ammonium hydroxide was over, the deep blue solution was cooled at ice-bath temperature for ca. 15 min. An excess of alcohol was then added to the cold solution with stirring whereupon the deep blue microcrystalline  $\text{A}_2[\text{V}(\text{O}_2)_3\text{F}]$  was obtained in a very high yield. The reaction container was allowed to cool for ca. 30 min, and the compound was then separated by centrifugation, washed several times with alcohol, and finally dried in vacuo over phosphorus pentoxide. The specific gram amounts of the reagents used and the yields of various alkali-metal and ammonium triperoxyfluorovanadates(V) are reported in Table I.

**Elemental Analyses.** Vanadium was estimated volumetrically, after the peroxy oxygen was expelled, by titration with standard potassium permanganate solution. A near-boiling vanadium(V) solution was treated with a stream of sulfur dioxide for ca. 10 min and then with a rapid stream of carbon dioxide to expel any excess of sulfur dioxide. The vanadium(IV) solution was then cooled to ca. 80 °C and titrated with standard potassium permanganate.<sup>8</sup> The peroxide content of

- (1) N. Vuletic and C. Djordjevic, *J. Chem. Soc.*, 1137 (1973).
- (2) S. Yamada, Y. Ukei, and H. Tanaka, *Inorg. Chem.*, **15**, 964 (1976).
- (3) S. Funahashi, K. Harraguchi, and M. Tanaka, *Inorg. Chem.*, **16**, 1349 (1977).
- (4) K. Wiegardt, *Inorg. Chem.*, **17**, 57 (1978).
- (5) U. Quilitzsch and K. Wiegardt, *Inorg. Chem.*, **18**, 869 (1979).
- (6) S. Funahashi, K. Ishihara, and M. Tanaka, *Inorg. Chem.*, **20**, 51 (1981).
- (7) M. K. Chaudhuri and S. K. Ghosh, *Polyhedron*, in press.

- (8) M. C. Steele and F. M. Hall, *Anal. Chim. Acta*, **9**, 384 (1953).