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	$10^{-4}k$, $M^{-2}\ s^{-1}$	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

[a] 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

$$k_2 = 10^{10.2\pm0.8} \exp [(-7200 \pm 1000 \text{ cal})/RT]$$

A plot of $\ln (k_2/T)$ vs. $1/T$ gives an activation enthalpy and entropy of 6.6 ± 1.0 kcal and −14 ± 4 cal/K, respectively, for the slow step. A parallel analysis by ourselves of Wilkins' data[4] 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.[12]

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. $HCrO_4^-$, 15596-54-0; H_2O_2, 7722-84-1; $HCrO_6^-$, 40330-52-7.

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(12) It should be noted that Orhanovic and Wilkins[5] have reported an enthalpy and entropy of activation for $CrO_5{\cdot}H_2O$ 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 $\Delta H^{\circ\ddagger}$ and $\Delta S^{\circ\ddagger}$ would not be comparable to our own.

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Homolytic Decomposition of Tertiary Organochromium(III) Complexes and Evidence for Their Decomposition via Reactions with Aliphatic Free Radicals. A Pulse Radiolysis Study[1]

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Received December 8, 1981

The rates of homolytic decomposition of $Cr-C(CH_3)_2OH^{2+}$, $Cr-C(CH_3)_2CO_2H^{2+}$, and $Cr-C(CH_3)_2CN^{2+}$ are 0.15 s^{-1}, 4 s^{-1}, and $10^4 < k < 10^6\ s^{-1}$, respectively. The reaction of some aliphatic free radicals, $\cdot R$ with $Cr^{III}-R$ complexes is very fast, $k_3 \geq 10^8\ M^{-1}\ s^{-1}$. The rate of reaction of $Cr^{2+}(aq)$ with H_2O_2 is $k_{16} = (3.7 \pm 0.7) \times 10^4\ M^{-1}\ s^{-1}$ in good accord with the literature value. These results are discussed in detail.

Introduction

Saturated aliphatic free radicals are known to react with $Cr^{2+}(aq)$ to form organochromium(III) complexes:[3,4]

$$Cr^{2+}(aq) + \cdot R \rightarrow Cr^{III}-R \qquad (1)$$

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

$$Cr^{III}-R \xrightarrow{H_2O} Cr^{III}(aq) + RH \qquad (2)$$

Recently Espenson and co-workers have shown that in the presence of efficient scavengers for $Cr^{2+}(aq)$ and/or $\cdot R$ (α-hydroxyalkyl)- and (α-alkoxyalkyl)chromium(III) complexes decompose homolytically.[5] The results indicate that the rate of homolysis increases with the introduction of steric hindrance to the chromium–carbon bond.[5] In another study Espenson[6] reported the formation of $Cr-CH_2CN^{2+}$, $Cr-CH_2CH_2CN^{2+}$, and $Cr-CH_2CH(CH_3)CN^{2+}$, which are all relatively stable in aqueous solutions. However, the formation of $Cr-CH(CH_3)CN^{2+}$ and $Cr-C(CH_3)_2CN^{2+}$ 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.[6]

We decided to try to measure the rates of homolysis of $Cr-CH(CH_3)CN^{2+}$ and $Cr-C(CH_3)_2CN^{2+}$ using the pulse radiolytic technique, which enables the observation of short-lived intermediates.[7,8] For comparison we decided to measure also the rates of homolysis of $Cr-C(CH_3)_2CO_2^+$ and $Cr-C(CH_3)_2OH^{2+}$ (the latter was measured in order to check the technique). We were unable to measure the rate of homolysis of $Cr-CH(CH_3)CN^{2+}$ but report here the rates of homolysis of the other complexes, which increase along the series Cr–

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(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.

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Table I. Rates of Reactions between $Cr^{2+}(aq)$ and H_2O_2, k_{16}

	$10^{-4}k_{16}$, $M^{-1}\ s^{-1}$	
organic solute	excess $Cr^{2+}(aq)$	excess H_2O_2[a]
CH_3CN	4.0 ± 0.4	3.2 ± 0.4
CH_3CH_2CN	4.5 ± 0.8	7.5 ± 0.8
$CH(CH_3)_2CN$	3.0 ± 0.4	6.3 ± 1.0
$CH(CH_3)_2CO_2H$		8.0 ± 2.0

[a] 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_{-1}, s^{-1}	Cr complex	k_{-1}, s^{-1}
$Cr–CH(CH_3)_2^{2+}$	2.4×10^{-4}[a]	$Cr–C(CH_3)_2CO_2H^{2+}$	4[c]
$Cr–C(CH_3)_2OH^{2+}$	0.13[b]	$Cr–C(CH_3)_2CN^{2+}$	$10^4 \leqslant k_{-1} \leqslant 10^6$[c]

[a] Reference 27 in ref 5. [b] Reference 5. [c] This work.

$CH(CH_3)_2^{2+}$, $Cr–C(CH_3)_2OH^{2+}$, $Cr–C(CH_3)_2CO_2^{+}$, and $Cr–C(CH_3)_2CN^{2+}$.

The results obtained also corroborate the earlier reported rate of reaction of $Cr^{2+}(aq)$ with H_2O_2[9] and indicate that aliphatic free radicals react with organochromium(III) complexes via

$$Cr^{III}–R + \cdot R' \rightarrow Cr^{2+}(aq) + R–R' \text{ or other decomposition products} \quad (3)$$

The rates of reaction 3 are relatively high, and the products of reactions were not isolated.[10]

Experimental Section

Materials. Chromous perchlorate solutions were prepared by dissolving high purity grade chromium powder in dilute $HClO_4$ 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 (1.0×10^3)–(1.3×10^4) 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.[12,13] 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[7]

$$H_2O \xrightarrow{\gamma, e^-} e_{aq}^-, \cdot OH, \cdot H, H_2, H_2O_2 \quad (4)$$

The primary products are formed with yields of $G_{e_{aq}^-} = G_{OH} = 2.65$, $G_H = 0.60$, $G_{H_2} = 0.45$, and $G_{H_2O_2} = 0.75$.[7] (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.[7]

In acidic solutions containing $Cr^{2+}(aq)$, $Cr^{3+}(aq)$, H_2O_2, and organic solutes of the general formula CH_3CHRX (where R ≡ CH_3 or H and X ≡ OH, CN, or CO_2H) reactions 1–3 and reactions 5–17 have to be considered. The rates of reaction

$$Cr^{3+}(aq) + e_{aq}^- \rightarrow Cr^{2+}(aq) \qquad k_5 = 6.0 \times 10^{10}\ M^{-1}\ s^{-1}\ {}^{14,15} \quad (5)$$

$$Cr^{2+}(aq) + e_{aq}^- \rightarrow Cr^{+}(aq) \qquad k_6 = 4.2 \times 10^{10}\ M^{-1}\ s^{-1}\ {}^{14} \quad (6)$$

$$H_3O^{+}(aq) + e_{aq}^- \rightarrow H \qquad k_7 = 2.3 \times 10^{10}\ M^{-1}\ s^{-1}\ {}^{16} \quad (7)$$

$$H_2O_2 + e_{aq}^- \rightarrow OH + OH^-(aq) \qquad k_8 = 1.2 \times 10^{10}\ M^{-1}\ s^{-1}\ {}^{16} \quad (8)$$

$$Cr^{2+}(aq) + H \rightarrow Cr^{III}–H \qquad k_9 = 1.5 \times 10^{9}\ M^{-1}\ s^{-1}\ {}^{17} \quad (9)$$

$$Cr^{III}–H + H_3O^{+}(aq) \rightarrow Cr^{3+}(aq) + H_2 \qquad k_{10} = 1.8 \times 10^{4}\ M^{-1}\ s^{-1}\ {}^{17} \quad (10)$$

$$H_2O_2 + H \rightarrow H_2O + \cdot OH \qquad k_{11} = 6.6 \times 10^{7}\ M^{-1}\ s^{-1}\ {}^{18} \quad (11)$$

$$CH_3CHRX + H \rightarrow H_2 + \cdot CR(CH_3)X \text{ or } \cdot CH_2CHRX \quad (12)$$

(the yield of $\cdot CR(CH_3)X$ is considerably larger than that of $\cdot CH_2CHRX$)

$$Cr^{2+}(aq) + \cdot OH \rightarrow Cr^{3+}(aq) \qquad k_{13} = 1.2 \times 10^{10}\ M^{-1}\ s^{-1}\ {}^{19} \quad (13)$$

$$H_2O_2 + \cdot OH \rightarrow H_2O + HO\cdot_2 \qquad k_{14} = 2.2 \times 10^{7}\ M^{-1}\ s^{-1}\ {}^{20} \quad (14)$$

$$CH_3CHRX + \cdot OH \rightarrow H_2O + \cdot CR(CH_3)X \text{ or } \cdot CH_2CHRX \quad (15)$$

(the yield of $\cdot CR(CH_3)X$ is considerably higher than that of $\cdot CH_2CHRX$)

$$Cr^{2+}(aq) + H_2O_2 \rightarrow Cr^{3+}(aq) + OH^- + \cdot OH \qquad k_{15} = 2.7 \times 10^{4}\ M^{-1}\ s^{-1}\ {}^{9} \quad (16)$$

$$2R\cdot \xrightarrow{H_2O} R_2 \text{ or } RH + ROH \quad (17)$$

(where $\cdot R = \cdot CR(CH_3)X$ or $\cdot CH_2CHRX$; when a more accurate definition of $\cdot R$ will be required, we will use the notation $\cdot R_1 = \cdot CR(CH_3)X$ and $\cdot R_2 = \cdot CH_2CHRX$)

of e_{aq}^- with CH_3CHRX,[16] of H and ·OH with $Cr^{3+}(aq)$,[18,20] and of the free radicals with H_2 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_2O_2 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 $\cdot C(CH_3)_2OH$ with H_2O_2, $k = 5 \times 10^5\ M^{-1}\ s^{-1}$, has been reported.[21] The other radicals used are known to be weaker reducing agents, and therefore their rates

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

(10) The observation that pinacol is formed via $Cr–C(CH_3)_2OH^{2+} + \cdot C(CH_3)_2OH \rightarrow Cr^{2+} + (CH_3)_2C(OH)C(OH)(CH_3)_2$[11] 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 $\cdot C(CH_3)_2OH$ free radicals.

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

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

(15) The rate reported is for $Cr(H_2O)_5OH^{2+}$; that for $Cr(H_2O)_6^{3+}$ 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*.

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(18) Anbar, M.; Farhataziz; 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) Farhataziz; 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.

of reaction with H_2O_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) × 10^{-4} M Cr^{2+}(aq) at pH 1.0 and 2.0 were irradiated. Under these conditions all the ·OH radicals react via reaction 15 to form the free radicals ·R, and all the e_{aq}^- are transformed into ·H atoms via reaction 7. The fate of the ·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 Cr^{III}–R, reaction 1. We hoped to follow now the decomposition of Cr^{III}–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 H_2O_2 formed by the pulse, eq 4, and Cr^{2+}(aq) occurs. The ·OH radicals formed react via reaction 15 followed by reaction 1 to form an additional amount of Cr^{III}–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.[9]

B. Solutions containing 1 × 10^{-2} M Cr^{3+}(aq) and 0.1–0.5 M of the organic solute at pH 2.65 with 0–5 × 10^{-3} M H_2O_2 were irradiated. Under these conditions most of the hydrated electrons reduce Cr^{3+}(aq), producing Cr^{2+}(aq), reaction 5, and only some disappear via reactions 7 or 8. Thus the Cr^{2+}(aq) formed reacts with ·R, formed by reaction 15, to form Cr^{III}–R. The yield of ·H atoms in this system is small, and indeed reaction 10 was not observed under these conditions. The yield of Cr^{2+}(aq) is somehwat smaller than that of ·R, but as k_1 is considerably lower than k_{17},[22] some Cr^{2+}(aq) remains in the solutions after all the ·R radicals reacted. When H_2O_2 is added to the solution, this excess of Cr^{2+}(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 Cr^{III}–R corresponds to $2k_{16}$.

If Cr^{III}–R_1 decomposes homolytically, the following reactions have to be considered:

$$\mathrm{Cr^{III}\text{–}R_1} \underset{k_1}{\overset{k_{-1}}{\rightleftarrows}} \mathrm{Cr^{2+}(aq)} + \cdot\mathrm{R_1} \tag{1a}$$

$$2\mathrm{R_1} \rightarrow (\mathrm{R_1})_2 \text{ or } \mathrm{HR_1} + \mathrm{HOR_1} \tag{17}$$

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

$$-\frac{\mathrm{d}[\mathrm{Cr^{III}\text{–}R_1}]}{\mathrm{d}t} = k_{17}\frac{k_{-1}^{\,2}}{k_1^{\,2}}\,\frac{[\mathrm{Cr^{III}\text{–}R}]^2}{[\mathrm{Cr^{2+}}]^2} \tag{18}$$

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

$$\cdot\mathrm{R_1} + \mathrm{Cr^{III}\text{–}R_1} \xrightarrow{k_{3a}} \text{products} \tag{3a}$$

$$\cdot\mathrm{R_1} + \mathrm{Cr^{III}\text{–}R_2} \xrightarrow{k_{3b}} \text{products} \tag{3b}$$

have to be taken in account. Assuming the steady-state assumption for $\cdot R_1$ and neglecting reaction 17, as $[Cr^{III}\text{–}R] >> [\cdot R_1]$, one obtains

$$-\frac{\mathrm{d}[\mathrm{Cr^{III}\text{–}R_1}]}{\mathrm{d}t} = \frac{2k_{-1}k_{3a}[\mathrm{Cr^{III}\text{–}R_1}]^2 + k_{-1}k_{3b}[\mathrm{Cr^{III}\text{–}R_1}][\mathrm{Cr^{III}\text{–}R_2}]}{k_1[\mathrm{Cr^{2+}(aq)}] + k_{3a}[\mathrm{Cr^{III}\text{–}R_1}] + k_{3b}[\mathrm{Cr^{III}\text{–}R_2}]} \tag{19}$$

In the presence of excess H_2O_2 the concentration of Cr^{2+}(aq) is low, due to reaction 16, and the rate of decomposition of Cr^{III}–R_1 will approach $2k_{-1}[Cr^{III}\text{–}R_1]$.

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

2-Propanol. When solutions containing excess Cr^{2+}(aq) were irradiated, the lifetime of $Cr\text{–}C(CH_3)_2OH^{2+}$ exceeded 1 min, even when low [Cr^{2+}(aq)], i.e., 1 × 10^{-4} M was used. When solutions containing 3.5 × 10^{-3} M $Cr(ClO_4)_3$, 0.1 M $CH(CH_3)_2OH$, and (3–10) × 10^{-2} M H_2O_2 at pH 3.3 were irradiated, the lifetime of the transient was considerably shorter, obeying a first-order rate law independent of [H_2O_2], with $k_{-1}(Cr\text{–}C(CH_3)_2OH^{2+})$ = 0.15 ± 0.05 s^{-1} in very good agreement with the results of Espeson et al.[5,6] Surprisingly enough similar results were obtained when no H_2O_2 was added to the solutions; pulses producing ca. 1.5 × 10^{-5} M Cr^{2+} and ca. 2.0 × 10^{-5} M $\cdot C(CH_3)_2OH$ were used. The kinetics observed under these conditions obeyed a first-order rate law with k = 0.020 ± 0.005 s^{-1}. The first-order rate law indicates that the decomposition reactions obey the rate law (19) with $k_1[Cr^{2+}(aq)] \leq k_3[Cr\text{–}C(CH_3)_2OH^{2+}]$ 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.[24] Similar reactions were observed for other systems containing σ carbon–metal bonds in aqueous solutions.[25]

Acetonitrile. When solutions containing (2–10) × 10^{-4} M Cr^{2+} and 0.5 M CH_3CN 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 $Cr\text{–}CH_2CN^{2+}$[6] remains in the solution. The first reaction observed is the formation of $Cr\text{–}H^{2+}$ (see below) and $Cr\text{–}CH_2CN^{2+}$. As ca. two-thirds of the absorption formed in this step, as measured at 290 nm, is due to $Cr\text{–}H^{2+}$, the rate observed corresponds to that of reaction 9. The results suggest, however, that $k_1(\cdot CH_2CN)$ 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 [H_3O^+], k = (1.3 ± 0.3) × 10^4 M^{-1} 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 [Cr^{2+}(aq)]; we attribute this process to reaction 16 and obtain k_{16} = (4.0 ± 0.4) × 10^4 M^{-1} s^{-1}. The same three processes were also observed in solutions containing 1.0 × 10^{-2} M Cr^{3+} and 0.5 M CH_3CN at pH 2.65 with (1–5) × 10^{-3} M H_2O_2. From this system we obtain k_{16} = (3.2 ± 0.4) × 10^4 M^{-1} s^{-1}. We observed no reactions due to the radical $CH_3C(OH){=}\dot{N}$.[6]

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 $Cr\text{–}CH_2CH_2CN^{2+}$ and/or $Cr\text{–}CH(CH_3)CN^{2+}$ relative to that of $Cr\text{–}H^{2+}$ is much higher. Thus we were able to determine k_1 in this system, $k_1(Cr^{2+} + \cdot CH_2CH_2CN/\cdot CH(CH_3)CN)$ = (2.3 ± 0.3) × 10^8 M^{-1} 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

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[22] The specific rates of reaction 1 are reported below, and k_{17} = (1–3) × 10^9 M^{-1} s^{-1} for most noncharged saturated aliphatic radicals.[23]

[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 $k_{10} = (1.4 \pm 0.3) \times 10^4\ \mathrm{M^{-1}\ s^{-1}}$ and $k_{16} = (7.5 \pm 0.8) \times 10^4\ \mathrm{M^{-1}\ s^{-1}}$ from solutions with excess H_2O_2 and $k_{16} = (4.5 \pm 0.8) \times 10^4\ \mathrm{M^{-1}\ s^{-1}}$ from solutions with excess 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 $Cr{-}CH(CH_3)CN^{2+}$,[6] 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 $CH(CH_3)_2$ and $(2{-}10) \times 10^{-4}$ M Cr^{2+} at $1.0 \le \mathrm{pH} \le 2.0$ 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 $[Cr^{2+}(aq)]$. From the results we calculate $k_1(Cr^{2+}(aq) + {\cdot}C(CH_3)_2CN/{\cdot}CH_2CH(CH_3)CN) = 1.9 \times 10^8\ \mathrm{M^{-1}\ s^{-1}}$. 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 $k/[(\Delta\epsilon)l] = 5 \times 10^4$ and 1.25×10^5 for $[Cr^{2+}(aq)] = 1 \times 10^{-3}$ M and 5×10^{-4} M, respectively (first-order rate law plots give $k \approx 2.1 \times 10^3$ and $2.8 \times 10^3\ \mathrm{s^{-1}}$ for the same solutions). At pH 2.0 however the decomposition reaction is split into two consectuvie 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 $k \approx 8 \times 10^3\ \mathrm{s^{-1}}$. The second one obeys a first-order rate law with $k = (1.4 \pm 0.3) \times 10^2\ \mathrm{s^{-1}}$, which suggests that the reaction observed is reaction 10, which has a rate of $1.8 \times 10^3\ \mathrm{s^{-1}}$ at pH 1.0[17] 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 $Cr{-}C(CH_3)_2CN^{2+}$. To calculate k_{-1} for this system, one can use eq 18 assuming $k_{17} = 2 \times 10^9\ \mathrm{M^{-1}\ s^{-1}}$ and $\epsilon_{290}(Cr{-}R) \approx 1000\ \mathrm{M^{-1}\ cm^{-1}}$,[26] which results in $k_{-1} \approx 5 \times 10^7\ \mathrm{s^{-1}}$. However, if $k_1/k_{-1} \approx 4$, then nearly no $Cr{-}R_1{}^{2+}$ would be formed under our experimental conditions. Furthermore the dependence of k on $Cr^{2+}(aq)$ is smaller than predicted. We used therefore eq 19 under conditions where $k_1[Cr^{2+}(aq)]$ 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 $k_3 \le 2 \times 10^9$, the diffusion-controlled limit for such reactions, clearly $k_{-1} > 10^4\ \mathrm{s^{-1}}$. As we observe the formation of $Cr{-}C(CH_3)_2CN^{2+}$, $Cr{-}R_1{}^{2+}$, in solutions containing 5×10^{-4} M $Cr^{2+}(aq)$ clearly $[R_1]/[Cr{-}R_1] \le 10$; therefore, $k_{-1} < 10^6\ \mathrm{s^{-1}}$. Thus we conclude that for this system $10^4 < k_{-1} < 10^6\ \mathrm{s^{-1}}$.

After the decomposition of $Cr{-}H^{2+}$ and $Cr{-}R_1{}^{2+}$ is over, we observe the formation of $Cr{-}R_2{}^{2+}$ due to reactions 16, 15, and 1. We calculate $k_{16} = (3.0 \pm 0.4) \times 10^4\ \mathrm{M^{-1}\ s^{-1}}$ from this system. In solutions containing $Cr^{3+}(aq)$ and H_2O_2 at pH 2.65 the homolytic decomposition is too fast to be observed and the only reaction observed, after the formation of $Cr{-}R_2{}^{2+}$ via reaction 1, is due to reaction 16. The results here give $k_{16} = (6.3 \pm 1.0) \times 10^4\ \mathrm{M^{-1}\ s^{-1}}$.

Isobutyric Acid. When solutions containing $(2{-}10) \times 10^{-4}$ M $Cr^{2+}(aq)$ and 0.1 M $CH(CH_3)_2CO_2H$ 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 $k_1(Cr^{2+}(aq) + {\cdot}C(CH_3)_2COOH/{\cdot}CH_2CH(CH_3)CO_2H) = (1.15 \pm 0.1) \times 10^8\ \mathrm{M^{-1}\ s^{-1}}$; 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 $k_{10} = (1.9 \pm 0.4) \times 10^4\ \mathrm{M^{-1}\ s^{-1}}$.

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 $Cr{-}C(CH_3)_2COH^{2+}$. The kinetics do not fit well either a first-order rate law, $k \approx 2.5\ \mathrm{s^{-1}}$, or a second-order rate law, $k/\epsilon l \simeq 40\ \mathrm{s^{-1}}$. The rate seems to be nearly independent of $[Cr^{2+}(aq)]$. These results suggest that eq 19 describes best the results and that in this case the term $k_1[Cr^{2+}(aq)]$ is not the major term in the denominator. Again, as the relative yields of ${\cdot}C(CH_3)_2CO_2H$ and ${\cdot}CH_2CH(CH_3)CO_2H$ and the molar absorption coefficients of the transients are unknown, k_{-1} can only be estimated from these results, $k_{-1} \approx 10\ \mathrm{s^{-1}}$. (The formation of $Cr{-}R^{2+}$, 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 1×10^{-2} M $Cr^{3+}(aq)$, 0.1 M $CH(CH_3)_2CO_2H$, and $0{-}5 \times 10^{-3}$ M H_2O_2 at pH 2.65 were irradiated, the results are simpler. The first process observed after the formation of $Cr{-}R^{2+}$ is reaction 16, for which we calculate $k_{16} = (8 \pm 2) \times 10^4\ \mathrm{M^{-1}\ s^{-1}}$. This reaction is followed by the homolytic decomposition of $Cr{-}C(CH_3)_2CO_2H^{2+}$, which under these conditions obeys a first-order rate law with $k_{-1} = 4 \pm 2\ \mathrm{s^{-1}}$.

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 CH_3CN, k_{16} obtained from experiments with excess H_2O_2 is significantly larger than that obtained from experiments with excess $Cr^{2+}(aq)$. 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 $d[Cr{-}R]/dt = -d[Cr^{2+}]/2dt$, when excess H_2O_2 is present. When, however, $k_3[Cr{-}R]$ attains a value of the same order of magnitude as $k_1[Cr^{2+}]$, this assumption is no longer correct. This clearly happens earlier when excess H_2O_2 is used and $[Cr^{2+}(aq)]$ is low. When reaction 3 starts to compete with reaction 1, the apparent rate of reaction 16 increases as the maximal concentration of $Cr{-}R^{2+}$ is formed faster. These results are in accord with the conclusion, derived from the measurements of k_{-1} above, that $k_3 \ge 1 \times 10^8\ \mathrm{M^{-1}\ s^{-1}}$ for most of the systems studied. The results indicate that k_3 for ${\cdot}CH_2CN + Cr{-}CH_2CN^{2+}$ has a lower rate constant.

Thus we believe that $\overline{k_{16}} = (3.7 \pm 0.7) \times 10^4\ \mathrm{M^{-1}\ s^{-1}}$, obtained from the experiments with excess $Cr^{2+}(aq)$ and the ${\cdot}CH_2CN$ 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 $k_{16} = 2.7 \times 10^4\ \mathrm{M^{-1}\ s^{-1}}$.[9]

Rate of Homolytic Decomposition of Tertiary Chromium–Carbon σ 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 σ 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, ${\cdot}R_1$. This conclusion is in agreement with the relatively high rate of homolytic decomposition of the primary chro-

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(26) As the relative yields of ${\cdot}CH_2CH(CH_3)CN$ and ${\cdot}C(CH_3)_2CN$ are not known, we obtain only an approximate average molar absorption coefficient for the two complexes with chromium–carbon bonds.

mium–carbon bond in Cr–$CH_2C_6H_5^{2+}$[27] and the very low rate of homolysis of Cr–$CH(CF_3)OH^{2+}$.[5]

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 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. Cr–$CH(CH_3)_2^{2+}$, 60764-48-9; Cr–$C(CH_3)_2OH^{2+}$, 32108-93-3; Cr–$C(CH_3)_2CO_2H^{2+}$, 82494-81-3; Cr–$C(CH_3)_2CN^{2+}$, 82494-82-4; Cr–CH_2CN^{2+}, 76068-68-3; Cr–$CH_2CH_2CN^{2+}$, 76068-69-4; Cr–$CH(CH_3)CN^{2+}$, 82494-83-5; Cr^{2+}(aq), 20574-26-9; H_2O_2, 7722-84-1.

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Alkali-Metal and Ammonium Triperoxyfluorovanadates(V), $A_2[V(O_2)_3F]$

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Received March 1, 1982

Blue alkali-metal and ammonium triperoxyfluorovanadates(V), $A_2[V(O_2)_3F]$ (A = NH_4, Na, and K) have been synthesized by reacting V_2O_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 $[V(O_2)_3F]^{2-}$ 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.[1-6] It appears from the recent literature that studies of the kinetic behavior of peroxyvanadium(V) engage the attention of most of the research groups,[2-6] 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 oxydiperoxyfluorovanadates(V), $A_2[VO(O_2)_2F]$. The compounds $A_2[VO(O_2)_2F]$ were synthesized by performing the reactions over a limited range of concentration of alkaline medium.[7] 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), $A_2[V(O_2)_3F]$ (A = 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 $Hg[Co(NCS)_4]$ as the calibrant.

Synthesis of Alkali-Metal and Ammonium Triperoxyfluorovanadates(V), $A_2[V(O_2)_3F]$ (A = 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 V_2O_5 and dry fluoride AF (A = NH_4, Na, or K) were taken with maintenance of the molar ratio of V_2O_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 V_2O_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 = NH_4, Na, or K), with maintenance of the molar ratio of V_2O_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 $A_2[V(O_2)_3F]$ 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.[8] The peroxide content of

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