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The Cyclopentylpentaaquochromium(III) Ion: Synthesis, Characterization, and Kinetics of Acidolysis, Homolysis, and Electrophilic Cleavage Reactions

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The complex $[(H_2O)_5Cr\text{-c-}C_5H_9]^{2+}$ is formed in the reaction of Cr^{2+} with H_2O_2 in aqueous solution saturated with cyclopentane. Reaction of Cr^{2+} with cyclopentyl radical, a step observed directly by pulse radiolysis ($k = (8.0 \pm 1.0) \times 10^7\ M^{-1}\ s^{-1}$), yields $(H_2O)_5Cr\text{-c-}C_5H_9^{2+}$, the radical being formed by abstraction from the hydrocarbon with $HO\cdot$. The complex was isolated chromatographically and characterized by its absorption spectrum and the products of reactions (C_5H_9Br from Br_2, C_5H_9OH from homolysis in the presence of Fe^{3+} and Cu^{2+}). It decomposes by parallel unimolecular pathways of acidolysis ($\rightarrow CrOH^{2+} + \text{c-}C_5H_{10}$, $k_{298} = (4.86 \pm 0.12) \times 10^{-4}\ s^{-1}$, $\Delta H^{\ddagger} = 73.5 \pm 2.4$ kJ mol^{-1}, $\Delta S^{\ddagger} = -61.5 \pm 7.9$ J mol^{-1} K^{-1} and homolysis ($\rightarrow Cr^{2+} + \cdot C_5H_9$, $k_{298} = (1.07 \pm 0.16) \times 10^{-4}\ s^{-1}$, $\Delta H^{\ddagger} = 126 \pm 2.9$ kJ mol^{-1}, $\Delta S^{\ddagger} = 102.5 \pm 9.3$ J mol^{-1} K^{-1}), although the latter is a reversible and thermodynamically unfavorable process, which occurs only in the presence of oxidizing agents. The complex also reacts in bimolecular displacement reactions (S_E2 mechanism) with Hg^{2+} ($k_{298} = 1.08 \pm 0.20\ M^{-1}\ s^{-1}$), Br_2 ($k_{298} = 1.30 \pm 0.19 \times 10^4\ M^{-1}\ s^{-1}$), and I_2 ($k_{298} = 8.2\ M^{-1}\ s^{-1}$).

Existing methods[2-8] of preparing alkylpentaaquochromium(III) ions exploit capture by Cr^{2+} of a free radical, often generated from an appropriately constituted hydroperoxide. The sequence of events in eq 1–4 is typical. Various

$$Cr(H_2O)_6^{2+} + RC(CH_3)_2OOH \rightarrow (H_2O)_5CrOH^{2+} + RC(CH_3)_2O\cdot + H_2O \quad (1)$$

$$RC(CH_3)_2O\cdot \rightarrow (CH_3)_2CO + R\cdot \quad (2)$$

$$Cr(H_2O)_6^{2+} + R\cdot \rightarrow (H_2O)_5CrR^{2+} + H_2O \quad (3)$$

$$\text{net:}\quad 2Cr(H_2O)_6^{2+} + RC(CH_3)_2OOH + H^+ = Cr(H_2O)_6^{3+} + (H_2O)_5CrR^{2+} + (CH_3)_2CO + 2H_2O \quad (4)$$

side reactions,[4] particularly other reactions of the alkyloxy radical prior to the β-scission process[9] of eq 2, result in low yields in many instances. A further shortcoming of the method is the necessity of synthesizing the appropriate hydroperoxide, usually from the alcohol, which depends upon the latter being readily available.

We have explored the feasibility of an alternative method based on the reaction of chromium(II) with hydrogen peroxide in solutions containing (and probably saturated with) the desired hydrocarbon. The method we suggest was used for cases where R· = α-hydroxyalkyl (from alcohols)[6,7] and α-alkoxyalkyl (from ethers).[6] As a test case we chose to explore this method using cyclopentane to generate cyclopentyl radicals and thus $(H_2O)_5Cr\text{-c-}C_5H_9^{2+}$. The anticipated sequence of reactions is given by eq 5–8.

$$Cr(H_2O)_6^{2+} + H_2O_2 \rightarrow (H_2O)_5CrOH^{2+} + HO\cdot + H_2O \quad (5)$$

$$HO\cdot + \text{c-}C_5H_{10} \rightarrow \cdot C_5H_9 + H_2O \quad (6)$$

$$Cr(H_2O)_6^{2+} + \cdot C_5H_9 \rightarrow (H_2O)_5Cr\text{-c-}C_5H_9^{2+} + H_2O \quad (7)$$

$$\text{net:}\quad 2Cr(H_2O)_6^{2+} + H_2O_2 + \text{c-}C_5H_{10} + H^+ = Cr(H_2O)_6^{3+} + (H_2O)_5Cr\text{-c-}C_5H_9^{2+} + 3H_2O \quad (8)$$

The choice of cyclopentane is optimal because it is more water soluble (~0.01 M) than most hydrocarbons and because the equivalency of its 10 hydrogen atoms results in the formation of but one aliphatic radical. In addition, the cyclopentyl radical can be produced pulse radiolytically, thus providing the first evaluation of the rate constant for a reaction of Cr^{2+} with an alkyl radical, as had been done previously for aliphatic radicals derived from alcohols, ethers, and acids.[10]

The studies of the kinetics and mechanisms of the reactions of $Cr\text{-c-}C_5H_9^{2+}$ afford some interesting comparisons with other organochromium cations,[11] most notably with $CrCH(CH_3)_2^{2+}$.[5] Toward this end we have determined the rate constants for the acidolysis reaction[6,11] with H_2O and H_3O^+, the homolysis reaction,[5b,11] and the electrophilic cleavage reactions that occur with mercury(II)[3a] and with bromine.[3b,12] The reaction of Br_2 with $CrCH(CH_3)_2^{2+}$ was also studied to complete the series needed for comparison purposes.

Experimental Section

Preparation of $(H_2O)_5Cr\text{-c-}C_5H_9^{2+}$. Chromium(II) perchlorate solutions were prepared by reduction of solutions of chromium(III)

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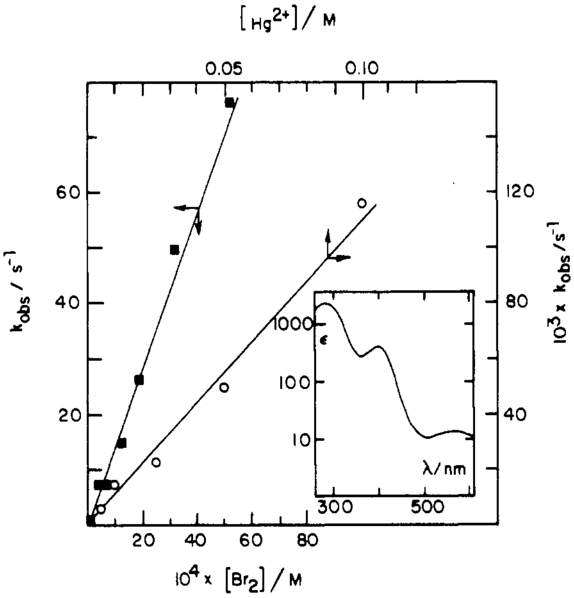

Figure 1. Linear variation of the pseudo-first-order rate constant for the reactions of $(H_2O)_5Cr\text{-}c\text{-}C_5H_9^{2+}$ with Hg^{2+} (circles) and Br_2 (squares). Note the different scales for the two reactions. The inset shows the UV–visible spectrum of the organochromium complex.

perchlorate in dilute, aqueous perchloric acid with amalgamated zinc and by dissolution of chromium metal in dilute perchloric acid. This reaction and subsequent procedures were conducted under Cr^{2+}-scrubbed nitrogen or argon because Cr^{2+} and this organochromium complex, like the 2-propyl complex,[5] are oxygen sensitive. Other reagents were prepared by standard methods.[3,5b,11] Solutions containing cyclopentylpentaaquochromium(2+) ion were prepared by injecting a roughly stoichiometric amount of Cr^{2+} into a solution of hydrogen peroxide (~0.01 M) saturated with cyclopentane.

The complex was isolated and purified by ion-exchange chromatography on Sephadex SP-C25. The column was maintained near 0 °C by circulating ice water, the complex being eluted with 0.25 M sodium perchlorate or perchloric acid to yield solutions containing some 0.002–0.004 M $Cr\text{-}c\text{-}C_5H_9^{2+}$ (~10% of theoretical according to eq 8). The UV–visible absorption spectrum is typical of other organochromium complexes,[8,10] with maxima at 400 nm (ϵ 413 ± 6 M^{-1} cm^{-1}) and 287 nm (2427 ± 35 M^{-1} cm^{-1}) as shown in Figure 1 (inset).

Reactions and Kinetics. Several different reactions were followed spectrophotometrically by monitoring the timed decrease in the absorbance of the organochromium complex at either or both of its absorption maxima. Ionic strength was maintained at 1.0 M with lithium perchlorate and perchloric acid. A Cary 219 spectrophotometer was used for the slower reactions and a digitized Durrum D-110 stopped-flow instrument for the more rapid ones. The reactions followed first-order or pseudo-first-order kinetics. The rate constants were calculated from the kinetic data by using standard methods and were independent of the monitoring wavelength.

Products. Gas chromatography was used to determine the organic products, with Perkin-Elmer 3920 B and Varian Model 3700 instruments with linear temperature programming and flame ionization detectors. Columns were packed with 5% FFAP or with 5% OV-101. The products were extracted either with methylene chloride or 1:9 pentane–ether. The retention times were confirmed with the authentic materials.

Pulse Radiolysis. The pulse radiolysis experiments were carried out at 22 ± 2 °C with use of 0.1–1.0-μs, 5-MeV, 200-mA pulses from the linear electron accelerator at the Hebrew University of Jerusalem. Details of these determinations and data analysis have been given elsewhere.[10,13]

Results

Kinetics of Formation of $(H_2O)_5Cr\text{-}c\text{-}C_5H_9^{2+}$. The primary processes in radiation chemistry[14] produce e_{aq}^-, HO·, and H·.

Table I. Kinetics[a] of Acidolysis of $(H_2O)_5Cr\text{-}c\text{-}C_5H_9^{2+}$

$[H_3O^+]$/ M	10^4k_{obsd}/ s^{-1}	$[H_3O^+]$/ M	10^4k_{obsd}/ s^{-1}
0.050	4.74	0.900	4.95
0.100	4.91	0.99	4.92
0.500	4.67	0.99	4.97
			av 4.86 ± 0.12

[a] At 25.0 °C and 1.00 M ionic strength. Solutions were free of oxygen and contained ~10^{-4} M Cr^{2+}.

These experiments were done at pH 3.3–4.0 in solutions saturated with nitrous oxide, ensuring quantitative conversion of e_{aq}^- to HO·. The hydroxyl radical reacts with cyclopentane as in eq 6, and H· reacts both with cyclopentane and with Cr^{2+}.[14b,c] The subsequent reaction of Cr^{2+} with the cyclopentyl radical, eq 7, was monitored by following the absorption of the organochromium product. The pseudo-first-order rate constant is directly proportional to the chromium(II) concentration, of which four different values, (2–10) × 10^{-4} M, were used. The rate of reaction of eq 7 is thus

$$d[(H_2O)_5Cr\text{-}c\text{-}C_5H_9^{2+}]/dt = k_7[Cr(H_2O)_6^{2+}][\cdot C_5H_9] \quad (9)$$

The average rate constant is k_7 = (8.0 ± 1.0) × 10^7 M^{-1} s^{-1} at 22 ± 2 °C.

Kinetics of Acidolysis. Heterolytic cleavage of the chromium–carbon bond occurs slowly in acidic solutions, forming $Cr(H_2O)_6^{3+}$ and cyclopentane (eq 10). So that only this

$$(H_2O)_5Cr\text{-}c\text{-}C_5H_9^{2+} + H_3O^+ = Cr(H_2O)_6^{3+} + c\text{-}C_5H_{10} \quad (10)$$

reaction might be observed, oxygen must be excluded and some low concentration of Cr^{2+} must be present to repress any contribution from the parallel homolytic pathway.[5b,11] A Cr^{2+} concentration on the order of 10^{-4} M is sufficient, and the reaction rates are independent of $[Cr^{2+}]$. The reaction follows first-order kinetics; variation of $[H^+]$ from 0.05 to 1.0 M at constant ionic strength (1.0 M) produced no effect (Table I). The rate law is

$$-d[Cr\text{-}c\text{-}C_5H_9^{2+}]/dt = k_A[Cr\text{-}c\text{-}C_5H_9^{2+}] \quad (11)$$

with k_A = (4.86 ± 0.12) × 10^{-4} s^{-1} at 25.0 °C.

Similar determinations were carried out at other temperatures between 20.2 and 50.4 °C; values of $10^4k_A/s^{-1}$ (T/°C) are as follows: 3.1 (20.23), 11.4 (33.45), 19.6 (37.7), and 53.9 (50.41). Analysis according to activated complex theory gives the activation parameters as $\Delta H^* = 73.5 \pm 2.4$ kJ mol^{-1} and $\Delta S^* = -61.5 \pm 7.9$ J mol^{-1} K^{-1}.

Kinetics of Homolysis. Addition of reagents that react rapidly with Cr^{2+} and/or the cyclopentyl radical draw homolytic decomposition, the reverse of eq 7, to completion. Among the reagents that are effective are Cu^{2+}, Fe^{3+}, and $(NH_3)_5CoX^{2+}$. The rate is independent of the concentration of such oxidizing scavengers, however, and follows first-order kinetics. The rate constant is the sum of the values for the two parallel pathways, acidolysis and homolysis. As before, the values are independent of $[H^+]$. The data (Table II) imply the rate law

$$-d[Cr\text{-}c\text{-}C_5H_9^{2+}]/dt = (k_A + k_H)[Cr\text{-}c\text{-}C_5H_9^{2+}] \quad (12)$$

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Table II. Kinetics[a] of Homolysis of $(H_2O)_5Cr\text{-}c\text{-}C_5H_9^{2+}$

$[H_3O^+]/M$	oxidizing scavenger,[b] concn/M	10^4k_{obsd}[c]$/s^{-1}$
0.100	Cu^{2+}, 0.0050	5.92
0.100	Cu^{2+}, 0.040	5.72
0.100	Fe^{3+}, 0.010	6.06
0.100	$(NH_3)_5CoF^{2+}$, 0.010	5.88
0.100	$(NH_3)_5CoCl^{2+}$, 0.003	6.01
0.100	$(NH_3)_5CoBr^{2+}$, 0.003	5.83
0.700	Fe^{3+}, 0.050	5.99
0.850	Cu^{2+}, 0.050	5.99
		av 5.93 ± 0.11

[a] At 25.0 °C and 1.00 M ionic strength. [b] The reagent added to react with Cr^{2+} and $c\text{-}C_5H_9\cdot$, the products of homolysis. [c] $k_{obsd} = k_A + k_H$ (see text); by difference, $k_H = (1.07 \pm 0.16) \times 10^{-4}$ s^{-1}.

Table III. Kinetics[a] of the Electrophilic Cleavage Reactions of Br_2 with $(H_2O)_5Cr\text{-}c\text{-}C_5H_9^{2+}$ and $(H_2O)_5CrCH(CH_3)_2^{2+}$

$[H_3O^+]/$ M	$10^3[Br_2]_0/$ M	$k_{obsd}/$ s^{-1}	$10^{-4}k_{Br_2}/$ $M^{-1}\ s^{-1}$
	(a) $(H_2O)_5Cr\text{-}c\text{-}C_5H_9^{2+}$		
1.00	0.12	(0.99)[b]	
1.00	0.55	7.05	1.29
1.00	0.71	7.21	1.02
1.00	1.3	14.9	1.15
1.00	1.9	26.1	1.38
0.50	3.2	49.8	1.56
1.00	5.2	73.2	1.41
			av 1.30 ± 0.19
	(b) $(H_2O)_5CrCH(CH_3)_2^{2+}$		
0.10	0.14	2.26	1.67
0.10	0.39	5.99	1.56
0.010	0.50	9.32	1.88
0.10	0.54	9.49	1.77
1.00	0.75	13.1	1.76
0.10	2.7	55.7	2.07
			av 1.79 ± 0.18

[a] At 25.0 °C and 1.00 M ionic strength. A stopped-flow technique with monitoring at 287 nm with $[CrR^{2+}]_0 \approx 10^{-5}$ M was used. [b] Excluded from average.

with $k_A + k_H = (5.93 \pm 0.11) \times 10^{-4}$ s^{-1} at 25.0 °C and 1.00 M ionic strength. By difference, $k_H = (1.07 \pm 0.16) \times 10^{-4}$ s^{-1}.

Values of $10^4k_H/s^{-1}$ (T/°C) determined at other temperatures are as follows: 0.55 (20.23), 4.49 (33.45), 9.90 (37.7), and 68.7 (50.2). The activation parameters are $\Delta H^\ddagger = 126.0 \pm 2.9$ kJ mol^{-1} and $\Delta S^\ddagger = 102.5 \pm 9.3$ J mol^{-1} K^{-1}.

Kinetics of Electrophilic Cleavage. The reactions occurring with bromine and iodine and with mercury(II) ions are given by eq 13 and 14.

$$(H_2O)_5Cr\text{-}c\text{-}C_5H_9^{2+} + X_2 \xrightarrow[X\,=\,Br,\,I]{H_2O} Cr(H_2O)_6^{3+} + c\text{-}C_5H_9X + X^- \quad (13)$$

$$(H_2O)_5Cr\text{-}c\text{-}C_5H_9^{2+} + Hg^{2+} \xrightarrow{H_2O} Cr(H_2O)_6^{3+} + HgC_5H_9^+ \quad (14)$$

Kinetic data for these reactions are given in Tables III–V, respectively. The bromine reaction rate had not been studied previously for the 2-propylchromium complex; in order to facilitate a complete comparison between the two, a series of experiments on the kinetics of the reaction of $CrCH(CH_3)_2^{2+}$ and Br_2 was also performed (Table III).

In the case of Br_2, the pseudo-first-order rate constants are directly proportional to $[Br_2]$ (Figure 1), as suggested by the rate law

$$-d[CrR^{2+}]/dt = k_{Br_2}[CrR^{2+}][Br_2] \quad (15)$$

Table IV. Kinetics[a] of the Electrophilic Cleavage Reactions of I_2 with $(H_2O)_5CrCH_3^{2+}$ and $(H_2O)_5Cr\text{-}c\text{-}C_5H_9^{2+}$

$10^4[I_2]/M$	k_{obsd}/s^{-1}	$10^{-4}k_{I_2}/M^{-1}\ s^{-1}$
	(a) $(H_2O)_5CrCH_3^{2+}$ [b]	
6.0	56.3	9.4
6.0	53.6	9.0
6.0	46.8	7.8
3.0	29.9	10.0
3.0	23.2	7.7
3.0	21.7	7.2
		av 8.5 ± 1.1
	(b) $(H_2O)_5Cr\text{-}c\text{-}C_5H_9^{2+}$ [c,d]	
10.3	9.02×10^{-3}	$k_{I_2} = 8.2$

[a] At 25.0 °C and 1.00 M ionic strength adjusted with aqueous $HClO_4$. [b] Stopped-flow technique with monitoring at 467 nm. [c] Cary 219 with monitoring at 467 nm. [d] $k_{I_2} = (k_{obsd} - k_A - k_H)/[I_2]_{av}$.

Table V. Kinetics[a] of the Electrophilic Cleavage Reaction of Hg^{2+} with $(H_2O)_5Cr\text{-}c\text{-}C_5H_9^{2+}$

$[H_3O^+]/M$	$[Hg^{2+}]/M$	$10^2k_{obsd}/s^{-1}$	k_{Hg}[b]$/M^{-1}\ s^{-1}$
0.94	0.0050	0.582	1.05
0.93	0.0100	1.44	1.38
0.88	0.0250	2.22	0.86
0.80	0.0500	4.97	0.98
0.65	0.100	11.6	1.15
			av 1.08 ± 0.20

[a] At 25.0 °C and 1.0 M ionic strength. The reactions were monitored with use of conventional spectrophotometry at 287 nm. [b] $k_{Hg} = (k_{obsd} - k_A - k_H)/[Hg^{2+}]_{av}$.

The high reaction rate precludes any appreciably contribution from acidolysis and homolysis. The average values at 25.0 °C and 1.0 M ionic strength are $k_{Br_2} = (1.30 \pm 0.19) \times 10^4$ M^{-1} s^{-1} (cyclopentyl) and $(1.79 \pm 0.18) \times 10^4$ M^{-1} s^{-1} (2-propyl).

The latter reaction was also studied as a function of temperature, $10^{-4}k_{Br_2}$ being 0.887 M^{-1} s^{-1} (10.2 °C), 2.13 (36.8 °C), and 3.03 (52.2 °C). These values yield $\Delta H^\ddagger = 19.6 \pm 2.4$ kJ mol^{-1} and $\Delta S^\ddagger = -99.3 \pm 7.8$ J mol^{-1} K^{-1}.

Data for reactions with iodine were obtained for both $Cr\text{-}c\text{-}C_5H_9^{2+}$ and $CrCH_3^{2+}$, the former requiring correction for acidolysis and homolysis. The rate constants at 25.0 °C and 1.0 M ionic strength are 8.2 and $(8.5 \pm 1.1) \times 10^4$ M^{-1} s^{-1}, respectively (Table IV).

The values of k_{obsd} for the reaction of $Cr\text{-}c\text{-}C_5H_9^{2+}$ with Hg^{2+} vary linearly with $[Hg^{2+}]$ (Table V and Figure 1). If the expected concentration-independent intercept corresponding to acidolysis plus homolysis is allowed for, then the rate law is

$$k_{obsd} = (k_A + k_H) + k_{Hg}[Hg^{2+}] \quad (16)$$

The rate constant at 25.0 °C and 1.0 M ionic strength is $k_{Hg} = 1.08 \pm 0.20$ M^{-1} s^{-1}. In comparison, earlier work[3a] gave $k_{Hg} = 1.56 \pm 0.01$ M^{-1} s^{-1} for $CrCH(CH_3)_2^{2+}$.

Reaction Products and Stoichiometry. With but one exception, chromium(III) in the form of $Cr(H_2O)_6^{3+}$ was produced in all the reactions studied, including the reactions with Br_2 (eq 13) in which no $(H_2O)_5CrBr^{2+}$ was isolated.[3b,12] A spectrophotometric titration gave $\Delta[Br_2]/\Delta[Cr\text{-}c\text{-}C_5H_9^{2+}] = 1.03$, confirming eq 13. These results are consistent with findings reported previously.[3b] Similar values were assumed for the reactions with I_2 and Hg^{2+}, in light of earlier work,[3] but were not checked. The one exception to formation of $Cr(H_2O)_6^{3+}$ is the homolytic cleavage reaction in the presence of $(NH_3)_5CoX^{2+}$ (X = Br, Cl, F), where CrX^{2+} was found. This is as expected from the reaction of the cobalt(III) complex with the Cr^{2+} produced from homolysis. The yield of Co^{2+} in experiments using $(NH_3)_5CoBr^{2+}$ amounts to 41% of the initial concentration of Cr-c-$C_5H_9^{2+}$. This compares to an expected yield of 37%, based on $100 \times 2k_H/(k_A + k_H)$. The latter expression assumes that the cyclopentyl radical as well as Cr^{2+} is oxidized by $(NH_3)_5CoBr^{2+}$. The product of the former reaction is cyclopentyl bromide (89%), confirming the reaction occurs via an inner-sphere mechanism (eq 17). This and similar reactions are currently under further investigation.

$$\text{c-C}_5\text{H}_9\cdot + \text{Co(NH}_3)_5\text{Br}^{2+} + 5\text{H}^+ \rightarrow \text{c-C}_5\text{H}_9\text{Br} + \text{Co}^{2+} + 5\text{NH}_4^+ \quad (17)$$

The amounts of the organic products were obtained by gas chromatography using as standards the known compounds present at comparable amounts, when extracted from solutions having the same electrolyte concentration. Copper(II) and iron(III) ions result in formation of cyclopentyl alcohol; the yields are 50% and 95% of the theoretical. In neither case was any other product found, and no cause other than accidental losses is apparent for the low yield from Cu^{2+}. Cyclopentyl bromide is the only organic product of the reaction with bromine as shown in eq 13.

Interpretation and Discussion

Formation of $(H_2O)_5$Cr-c-$C_5H_9^{2+}$. The synthetic steps and the mechanism by which they occur require little additional comment. This is the first instance in which an organochromium cation has been obtained from a hydrocarbon radical prepared from the parent hydrocarbon by the modified Fenton's reagent method. It should be noted that a procedure was recently devised[16] for $(H_2O)_5CrCH_3^{2+}$ based on the combination of Cr^{2+}, H_2O_2, and $(CH_3)_2SO$; in this case the radical-forming reaction is

$$\text{HO}\cdot + (\text{CH}_3)_2\text{SO} \rightarrow [(\text{CH}_3)_2\text{S(O}\cdot)\text{OH}] \rightarrow \text{CH}_3\text{SO}_2\text{H} + \cdot\text{CH}_3 \quad (18)$$

The methods are complementary, in that the combination of Cr^{2+}, H_2O_2, and CH_4 is not likely to be successful. The problem is a combined effect of the low water solubility of methane compared to that of cyclopentane and the slowness of the reaction of hydroxyl radical with methane (1.2×10^8 M^{-1} s^{-1})[17] as compared to its reaction with cyclopentane (eq 6, $k = 3.0 \times 10^9$ M^{-1} s^{-1}).[18] The reaction between HO· and CH_4 would occur too slowly, hydroxyl radicals being "wasted" in oxidizing Cr^{2+} to $Cr(H_2O)_6^{3+}$ ($k = 4.8 \times 10^9$ M^{-1} s^{-1}).[19]

The radiolytically evaluated rate constant for the coupling reaction between the cyclopentyl radical and chromium(II) ion is $k_7 = 8.0 \times 10^7$ M^{-1} s^{-1}. Substituted aliphatic radicals have rate constants between 3.4×10^7 (·$CH(CH_3)OC_2H_5$) and 3.5×10^8 M^{-1} s^{-1} (·CH_2CHO).[10] Perhaps the closest comparison to cyclopentyl, at least structurally, is the carbon-centered radical from dioxane, $\cdot\overline{\text{CHCH}_2\text{O(CH}_2)_2\text{O}}$. The value for it ($1.0 \times 10^8$ M^{-1} s^{-1}) and for k_7 are nearly the same, suggesting little kinetic influence from an ether linkage as compared to that from CH_2.

Acidolysis and Homolysis. The previously given arguments[5b,8,11] that the concurrent unimolecular reactions occurring are, in fact, correctly assigned to the processes of homolysis and acidolysis need not be repeated here. This pair of reactions affords a rare opportunity in an inorganic or organometallic compound for the comparison (Table VI) between the mechanisms taken by concurrent reactions of the same compound under the same conditions. The rate laws for the two reactions have the same kinetic form, eq 11 and 12, making this a perfectly valid comparison. The pair of activated complexes is isomeric, save possibly for a different involvement of solvent water molecules. Indeed, even the values of the rate constants k_A and k_H are similar at 25 °C.

Table VI. Comparison of Kinetic Parameters for the Acidolysis and Homolysis Reactions

kinetic parameter	acidolysis	homolysis
$10^4k_{298}/s^{-1}$	4.82 ± 0.13	1.10 ± 0.26
$\Delta H^{\ddagger}$/kJ mol^{-1}	73.5 ± 2.4	126.0 ± 2.9
$\Delta S^{\ddagger}$/J mol^{-1} K^{-1}	−61.5 ± 7.9	102.5 ± 9.3
k_{H_2O}/k_{D_2O}[a]	6.3	1.01

[a] The values given apply to the analogous reactions of $CrC(CH_3)_2OH^{2+}$,[21] although semiquantitative determinations for Cr-c-$C_5H_9^{2+}$ are in agreement (see text).

Associated with k_A and k_H, however, are activation parameters and deuterium isotope effects which are quite distinctive. The homolysis reaction occurs by chromium–carbon bond scission, evidently unassisted to any appreciable extent by compensating bond-making reactions. Associated with homolysis of Cr-c-$C_5H_9^{2+}$ is a large and positive entropy of activation, 103 J mol^{-1} K^{-1}. The value of $\Delta H^{\ddagger}$ is also large, 126 kJ mol^{-1}. Both factors are very much like those found for several other examples of homolytic dissociation of $(H_2O)_5CrR^{2+}$.[5b,8,11,20] Homolysis is an endothermic reaction, and as such the activated complex is expected by Hammond's postulate to resemble the products, Cr^{2+} and the cyclopentyl radical. The activation parameters are certainly consistent with that view and suggest that scission of the chromium–carbon bond is nearly complete at the transition state. The solvent deuterium isotope effect is negligible, the rate of homolysis being virtually unchanged in D_2O compared to that in H_2O. (Actually, this result pertains to $CrC(CH_3)_2OH^{2+}$,[21] but semiquantitative results suggest that it is true also for Cr-c-$C_5H_9^{2+}$.)

In contrast, the value of $\Delta S^{\ddagger}$ associated with k_A is negative, −62 J mol^{-1} K^{-1}. The mechanism of acidolysis[5b,6,10,11] involves electrophilic attack of a water molecule on the α-carbon atom. More specifically, a water molecule coordinated cis to the chromium–carbon bond has been suggested to be the reactive one,[8,10] rather than a solvent molecule. The ordering in the transition state implied by the negative activation entropy is consistent with the constriction implied in rate-limiting proton transfer from water. In keeping with this, substantial solvent isotope effects on the acidolysis of $(H_2O)_5CrR^{2+}$ complexes have been noted, $k_A(H_2O)/k_A(D_2O)$ being 6.1[22] or 6.3[23] (R = CH_3), 6.4 ($C(CH_3)_2OH$),[21] and 8.4 (CH_2OH).[22] The kinetic effect of D_2O on Cr-c-$C_5H_9^{2+}$ was examined only semiquantitatively, but again a substantial lowering of the acidolysis rate was noted.

The relative rates of acidolysis and homolysis (at 25 °C) are reversed for the structurally related 2-propyl and cyclopentyl complexes:

	$10^4k_H/s^{-1}$	$10^4k_A/s^{-1}$	k_H/k_A
Cr-c-$C_5H_9^{2+}$	1.07	4.86	0.22
$CrCH(CH_3)_2^{2+}$	1.78	1.07	1.66

The most significant difference is in the value of k_A. That the cyclopentyl complex, slightly more hindered to external attack than the 2-propyl complex (compare the k_{Hg} value as well), does not undergo acidolysis more slowly is supporting evidence

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Table VII. Logarithms of the Rate Constants for Hg^{2+}, Br_2, and I_2 with Various Pentaaquoorganochromium(III) Ions ($(H_2O)_5CrR^{2+}$)

R	log (k_E/M^{-1} s^{-1})		
	Hg^{2+} [a]	Br_2	I_2
CH_3	7.0	6.32	4.93
CH_2CH_3	5.15	5.69	
$CH_2CH_2CH_3$	4.54	5.99	
CH_2Ph	4.69	5.92	3.62[c]
$CH(CH_3)_2$	0.19	4.25	
c-C_5H_9	0.033	4.11	0.91

[a] References: c-C_5H_9, this work; all other alkyls, ref 3a. [b] References: c-C_5H_9 and $CH(CH_3)_2$, this work; all other alkyls, ref 3b. [c] Reference 24.

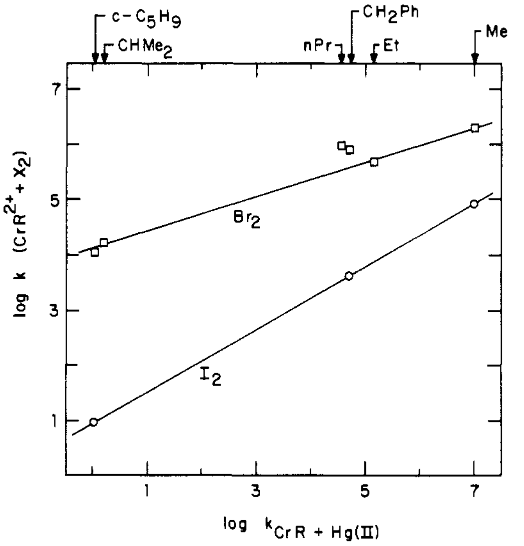

Figure 2. Correlation of the rate constant for reactions of various CrR^{2+} complexes with Br_2 and I_2, as compared to that for the reactions with Hg^{2+}. The coordinates for each point are (log $k^R{}_{Hg^{2+}}$, log $k^R{}_{X_2}$).

against attack of an external water molecule.

The rate constants reported here permit calculation of the equilibrium constant for the reversible homolytic dissociation equilibrium:

$$(H_2O)_5Cr\text{-c-}C_5H_9{}^{2+} + H_2O \underset{k_7}{\overset{k_H}{\rightleftharpoons}} Cr(H_2O)_6{}^{2+} + \cdot C_5H_9 \tag{19}$$

The kinetically determined value is $K_{eq} = k_H/k_7 = (1.3 \pm 0.2) \times 10^{-12}$ M at 25 °C, corresponding to $\Delta G°_{298} = 67.8$ kJ mol^{-1}. The value of $\Delta H°$, given by $H° = \Delta H^{\ddagger}{}_H - \Delta H^{\ddagger}{}_7$, can be calculated only if we estimate $\Delta H^{\ddagger}{}_7 \approx 0$. In that case $\Delta H° \approx 126$ kJ mol^{-1}, which may be taken (with suitable caution[11]) as an approximate measure of the chromium–carbon bond dissociation enthalpy.

Electrophilic Cleavage Reactions. Data are now available giving the rate constants for the three electrophiles Br_2, I_2, and Hg^{2+} reacting with various $(H_2O)_5CrR^{2+}$ complexes, from this and previous work,[3a,b,24] as summarized in Table VII. A linear free energy diagram, Figure 2, constructed from these data show a good correlation of the bromine and iodine electrophiles to the Hg^{2+} electrophile. The slopes of the lines (0.31 and 0.57, respectively) are a measure of the steric demand of the given electrophile relative to that of Hg^{2+}. Both bromine and iodine show a smaller steric deceleration than mercuric ion; as expected from the size of the molecules, the bromine's steric requirement is smaller than iodine's.

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Registry No. Cyclopentylpentaaquachromium(III) ion, 84559-49-9; chromium(II) perchlorate, 13931-95-8; hydrogen peroxide, 7722-84-1; cyclopentane, 287-92-3; copper(2+), 15158-11-9; iron(3+), 20074-52-6; pentaamminefluorocobalt(2+), 15392-06-0; bromine, 7726-95-6; iodine, 7553-56-2; mercury(2+), 14302-87-5; pentaaqua(1-methylethyl)chromium(2+), 60764-48-9; pentaamminechlorocobalt(2+), 14970-14-0; pentaamminebromocobalt(2+), 14970-15-1; deuterium, 7782-39-0; pentaaquamethylchromium(2+), 32108-96-6.

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Base Hydrolysis of $[Co(NH_3)_5X]^{n+}$—Capture of the Oxygen and Nitrogen of the Nitrite Ion

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Nitrite ion competition has been measured for the base hydrolysis reaction of a series of $[(NH_3)_5CoX]^{n+}$ ions (X = $CF_3SO_3^-$, $CH_3SO_3^-$, NO_3^-, $(CH_3)_2SO$, $OP(OCH_3)_3$, $OC(NH_2)_2$, and $OC(NH_2)N(CH_3)_2$) in 1.00 M $NaNO_2$. Contrary to previous reports, both O- and N-bonded $[(NH_3)_5Co(NO_2)]^{2+}$ are formed. A constant O-isomer/N-isomer ratio (67 ± 3% $CoONO^{2+}$, 33 ± 3% $CoNO_2{}^{2+}$) pertains for both anionic and neutral X. The total NO_2^- capture shows a slight dependence on the overall charge of the complex (7.0 ± 0.5% for 2+ cations, 8.3 ± 0.5% for 3+) but is less dependent on the nature of X. The results are consistent with a common, reactive intermediate of reduced coordination number, $[(NH_3)_4(NH_2)Co]^{2+}$, in the base hydrolysis process, provided the intermediate is considered to capture the environment of its precursor.

Introduction

The linkage isomerization of the oxygen-bonded nitrite complex $[(NH_3)_5CoONO]^{2+}$ to the nitrogen bound form $[(NH_3)_5CoNO_2]^{2+}$ has been reexamined recently, particularly in relation to a base-catalyzed path for the rearrangement.[2-4] The base hydrolysis reactions of $[(NH_3)_5CoX]^{n+}$ ions in the

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