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Pressure and Temperature Effects on the Rates of Concurrent Homolytic and Heterolytic Decomposition Pathways of Aqueous (2-Propyl- and 2-Hydroxyprop-2-yl)chromium(III) Ions

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Abstract: The volumes of activation ΔV^* for acid-independent heterolysis ("acidolysis") of $(H_2O)_5CrC(CH_3)_2OH^{2+}$ and $(H_2O)_5CrCH(CH_3)_2^{2+}$ in aqueous $HClO_4$ are +0.3 ± 0.2 and −0.2 ± 0.2 $cm^3\ mol^{-1}$, respectively, at ionic strength 1.0–1.1 mol L^{-1}. These data are consistent with separation of propanol and propane, respectively, from $(H_2O)_nCrOH^{2+}$ in the rate-determining step. For the concurrent homolytic pathways leading to Cr^{2+}(aq) and $\cdot C(CH_3)_2OH$ or $\cdot CH(CH_3)_2$, ΔV^* is +15.1 ± 1.6 $cm^3\ mol^{-1}$ (no significant pressure dependence, 0.1–100 MPa) and +26 ± 2 $cm^3\ mol^{-1}$ (low-pressure limit, decreasing with increasing pressure to 300 MPa), respectively. The larger ΔV^* values for homolysis relative to heterolysis, as well as the pressure dependence of ΔV^* for the homolysis of the 2-propyl complex, are ascribed in large part to massive desolvation, i.e., breakup of the solvent cage, as the organic radicals separate from Cr^{2+}. For the heterolysis of $(H_2O)_5CrCH(CH_3)_2^{2+}$, ΔH^* = 87 ± 3 kJ mol^{-1} and ΔS^* = −29 ± 10 J $K^{-1}\ mol^{-1}$; for homolysis, the corresponding data are 106 ± 1 kJ mol^{-1} and +42 ± 5 J $K^{-1}\ mol^{-1}$.

Espenson's recent review[2] has highlighted the important advances that have recently been made, largely in his own laboratory, toward the understanding of the aqueous reactions of organochromium(III) complexes of the type $(H_2O)_5CrR^{2+}$, which result from the reaction of aqueous chromium(II) and a carbon-centered free radical:

$$Cr(H_2O)_6^{2+} + R\cdot \rightarrow (H_2O)_5CrR^{2+} + H_2O \qquad (1)$$

The free radical R· may often be conveniently produced in situ by allowing H_2O_2 and $Cr(H_2O)_6^{2+}$ to react in the presence of the appropriate solute, such as 2-propanol (R = $(CH_3)_2COH$):[2-4]

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

$$HO\cdot + (CH_3)_2CHOH \rightarrow H_2O + \cdot C(CH_3)_2OH \qquad (3)$$

$$Cr(H_2O)_6^{2+} + \cdot C(CH_3)_2OH \rightarrow (H_2O)_5CrC(CH_3)_2OH^{2+} + H_2O \qquad (4)$$

In the case where R = 2-propyl, this reaction sequence is inapplicable because of the insolubility of RH, but the radical R· can be generated by reaction of $Cr(H_2O)_6^{2+}$ with 2,3-dimethyl-2-butyl hydroperoxide.[5,6]

$$Cr(H_2O)_6^{2+} + (CH_3)_2CH\text{-}C(CH_3)_2OOH \rightarrow (H_2O)_5CrOH^{2+} + (CH_3)_2CH\text{-}C(CH_3)_2O\cdot + H_2O \qquad (5)$$

$$(CH_3)_2CH\text{-}C(CH_3)_2O\cdot \rightarrow (CH_3)_2\dot{C}H + (CH_3)_2CO \qquad (6)$$

$$(CH_3)_2\dot{C}H + Cr(H_2O)_6^{2+} \rightarrow (H_2O)_5CrCH(CH_3)_2^{2+} + H_2O \qquad (7)$$

It is therefore to be expected that homolysis of the Cr–R bond, i.e., the reverse of reactions 4 and 7, should provide a possible mechanism for the decomposition of $(H_2O)_5CrR^{2+}$.

$$(H_2O)_5CrR^{2+} + H_2O \underset{k_{-H}}{\overset{k_H}{\rightleftharpoons}} Cr(H_2O)_6^{2+} + R\cdot \xrightarrow{k_P} \text{products} \qquad (8)$$

Because $(H_2O)_5CrR^{2+}$ may be regarded as a carbanion complex of chromium(III), however, the possibility exists of alternative heterolytic decomposition pathways (acidolysis) which may have acid-independent

$$(H_2O)_5CrR^{2+} + H_2O \xrightarrow{k_{1A}} Cr(H_2O)_5OH^{2+} + RH \qquad (9)$$

and/or acid-dependent

$$(H_2O)_5CrR^{2+} + H_2O + H^+ \xrightarrow{k_{2A}} Cr(H_2O)_6^{3+} + RH \qquad (10)$$

components. The relative importance of pathways 8, 9, and 10 varies widely with the nature of R.[2-7] For R = $C(CH_3)_2OH$, all three pathways can be observed. Homolysis (pathway 8) can be suppressed by addition of a sufficient excess of chromium(II),[2-4,7] and by choosing a sufficiently low hydrogen ion concentration (0.1 M or less; M = mol L^{-1} at 0.1 MPa and 294 K) the acid-independent heterolysis rate coefficient k_{1A} can be measured essentially independently of the acid-dependent component k_{2A}. Conversely, if a reagent is added which rapidly scavenges chromium(II) or R·, or both, the measured first-order homolysis rate coefficient will become equal to k_H, and the overall decomposition rate coefficient at low acidity becomes ($k_H + k_{1A}$) which, for R = $C(CH_3)_2OH$, effectively equals k_H.[2-4] Thus, in this case, k_{1A} and k_H can readily be measured separately, but k_H is sufficiently fast to require stopped-flow methods.

For R = $CH(CH_3)_2$, both k_{1A} and k_H are slow enough for measurement by conventional techniques, while k_{2A} is entirely negligible.[2,6] These experimental advantages are somewhat offset by the similarity of the k_{1A} and k_H values, which means that k_{1A} is never negligible and so k_H measurements are affected by uncertainties in k_{1A}. Furthermore, the longer time scale of these experiments increases the risk of interference from side reactions, and particularly stringent exclusion of contaminants such as oxygen[6] becomes essential.

Despite these experimental obstacles, we have undertaken to study the effects of pressure on k_H and k_{1A} for both $(H_2O)_5CrC(CH_3)_2OH^{2+}$ and $(H_2O)_5CrCH(CH_3)_2^{2+}$, since no volumes of activation ΔV^* have been reported so far[8] for homolyses of aqueous complex ions, and these particular species offer special opportunities to compare heterolyses and homolyses that proceed

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via isomeric transition states. The marked differences between the enthalpies ΔH^* and also the entropies ΔS^* of activation for homolysis and acidolysis of $(H_2O)_5CrC(CH_3)_2OH^{2+}$ show these isomeric transition state to be substantially different;[2,3] the corresponding parameters for the decomposition of $(H_2O)_5CrCH(CH_3)_2^{2+}$ are reported here for the first time, and they show similar trends. Volumes of activation can be expected to help elucidate the underlying differences in reaction mechanism.[8]

Experimental Section

Preparation and Reactions of $(H_2O)_5CrC(CH_3)_2OH^{2+}$. General experimental procedures were identical with those adopted before.[3,4] Chromium(II) perchlorate solutions were prepared by reduction of $Cr(ClO_4)_3$ (Ventron) over amalgamated zinc under the rigorous exclusion of oxygen. All solutions were deoxygenated by bubbling three-ring N_2 through for at least 20 min. H_2O_2 solutions were standardized iodometrically.[9] Chemicals of analytical reagent grade and doubly distilled water were used throughout the study. The UV-vis spectra of solutions of the 2-hydroxy-2-propylchromium(III) ion so prepared were identical with those reported by Espenson et al.[2,3]

Acidolysis reactions were studied on a Zeiss PMQ II spectrophotometer equipped with a thermostated (±0.1 °C) high-pressure cell.[10] Homolysis reactions were studied on a high-pressure stopped-flow instrument,[11] of which the temperature was controlled within 0.1 °C. The le Noble pill-box cell[12] and Kel-F syringes were filled with the appropriate solutions in a glovebag under N_2 atmosphere. First-order plots were linear for at least 3 half-lives in all cases.

Preparation and Reactions of $(H_2O)_5CrCH(CH_3)_2^{2+}$. All materials were prepared from Baker Analyzed or Fisher Certified reagents, except as indicated. Distilled water was further purified either by passage through Barnstead deionizer and organic removal cartridges or by redistillation from alkaline $KMnO_4$; the kinetic results were the same in either case. Chromium(III) perchlorate 9hydrate, made from CrO_3 by H_2O_2 reduction, was recrystallized from 2 M $HClO_4$, checked for purity spectrophotometrically, and analyzed for Cr before reduction to aqueous acidic Cr(II) with zinc amalgam under Cr(II)-scrubbed nitrogen. No reduction of the ClO_4^- was detectable after 30 min of reduction in contact with the Zn/Hg, but solutions for kinetic studies were not exposed to the amalgam longer than 10 min.

2,3-Dimethyl-2-butyl hydroperoxide was made from 2,3-dimethyl-2-butanol (Aldrich, >99%) by the method of Leslie and Espenson,[5] with the important modification that the cold dimethylbutanol was added to the reaction mixture over a period of *at least* 45 min while the temperature of the mixture was maintained at −2 to −5 °C. The product was freed of emulsified water by purging with dry nitrogen and was stored at 4 °C until required.

Solutions of $(H_2O)_5CrCH(CH_3)_2^{2+}$ for kinetic studies were prepared under O_2-free N_2, either directly in the optical cell or in a separate flask connected to the cell with PTFE tubing. For the studies of acidolysis, a solution containing the appropriate amounts of $Cr(ClO_4)_3$, $HClO_4$, and $LiClO_4$ was syringed through a serum cap into a flask containing deoxygenated zinc amalgam. When reduction to Cr(II) was complete, the solution was driven under slight excess pressure into a second flask (or the optical cell) containing the requisite amount of dimethylbutyl hydroperoxide. Reaction was complete on mixing, giving an intensely yellow solution. For studies of the combined acidolysis and homolysis reactions, either the calculated quantity of $Cu(ClO_4)_2$ solution was syringed into the organochromium solution or the latter was driven by slight N_2 pressure into a further oxygen-free flask containing solid $[Co(NH_3)_5Cl](ClO_4)_2$.[13] In some cases, the organochromium ion was purified by absorption on to Dowex 50W-X4 ion exchange resin (Li^+ form), washing with deoxygenated water, and rapid elution with $LiClO_4/HClO_4$ solution of the desired ionic strength, all at 0 °C. The solution had an absorption maximum at 401 nm (cf. 400 nm, reported[6]) and gave kinetic results which were identical with those obtained without resort to ion exchange purification.

Kinetic measurements were made by following the decay of the 400-nm absorption band, using a Cary Model 17H spectrophotometer. Temperature-dependence studies were made with ordinary cuvettes, sealed with serum caps and mounted in an aluminum block thermostated (±0.05 °C) with circulating water. Pressure-dependence measurements were carried out as described previously;[14] the mating surfaces of the quartz le Noble cell[12,15] were lightly coated with silicone grease, and the cell was loaded with solution and inserted into the thermally pre-equilibrated pressure vessel in a glovebag filled with Cr(II)-scrubbed nitrogen. The assembly was pressurized with optically transparent mineral oil (Exxon Marcol 70), and the reaction was monitored after allowing 40 min for full themal re-equilibration.

Table I. Rate Coefficients k_{obsd} as a Function of Pressure for the Acidolysis of $(H_2O)_5CrC(CH_3)_2OH^{2+\,a}$

pressure, MPa	10^3k_{obsd},[b] s^{-1}
5.0	1.33 ± 0.03
20.0	1.317 ± 0.004
30.0	1.34 ± 0.02
50.0	1.33 ± 0.02
70.0	1.33 ± 0.03
85.0	1.32 ± 0.01
100.0	1.31 ± 0.02
ΔV^*, $cm^3\ mol^{-1}$	+0.3 ± 0.2

[a] Temperature = 15.0 °C; wavelength = 410 nm; [2-PrOH] = 1 M; [H^+] = 0.1 M; ionic strength = 1.1 M ($NaClO_4$); [H_2O_2] = 4 × 10^{-3} M; [Cr(II)] = 0.05 M. [b] Mean value of three kinetic runs.

Table II. Rate Coefficients k_ob_{sd} as a Function of Pressure for the Homolysis of $(H_2O)_5CrC(CH_3)_2OH^{2+\,a}$

pressure, MPa	k_{obsd},[b] s^{-1}
1.0	0.218 ± 0.007
25.0	0.177 ± 0.004
50.0	0.165 ± 0.004
75.0	0.144 ± 0.006
100.0	0.112 ± 0.001
ΔV^*, $cm^3\ mol^{-1}$	+15.1 ± 1.6

[a] Temperature = 25.0 °C; wavelength = 400 nm; [2-PrOH] = 1 M; [H^+] = 0.1 M; ionic strength = 1.1 M ($NaClO_4$); [H_2O_2] = 0.05 M; [Cr(II)] = 5 × 10^{-3} M. [b] Mean value of six kinetic runs.

Results

In this article, uncertainty limits cited are standard deviations, except as noted.

Acidolysis of $(H_2O)_5CrC(CH_3)_2OH^{2+}$. According to the literature[3,4] the rate constants k_{1A} and k_{2A} for the acidolysis of $(H_2O)_5CrC(CH_3)_2OH^{2+}$ are 3.3 × 10^{-3} s^{-1} and 4.7 × 10^{-3} M^{-1} s^{-1}, respectively, at 25 °C. Since we were mainly interested in the acid-independent process, kinetic measurements were performed at [H^+] = 0.1 M, where this process predominates. The pressure-dependence study was done at 15 °C where the reaction has a half-life of ca. 8 min. The observed rate coefficients k_{obsd} (here, = k_{1A}) are summarized in Table I, from which it follows that k_{1A} is effectively independent of pressure—an unusual occurrence in high-pressure kinetics. The extrapolated k_{obsd} at 0.1 MPa is in excellent agreement with the value of 1.4 × 10^{-3} s^{-1} reported by Taube et al.[4] under identical conditions.

Homolysis of $(H_2O)_5CrC(CH_3)_2OH^{2+}$. Preliminary stopped-flow experiments on the homolysis of $(H_2O)_5CrC(CH_3)_2OH^{2+}$ at ambient pressure produced rate constants k_H significantly higher than those found by Espenson et al.[5] Various experiments were performed to resolve this discrepancy. Lower rate constants were observed from time to time, apparently depending on the nature of the Cr(II) solution, which contained Zn^{2+} and possibility chloride (from the reduction of ClO_4^-) impurities that may have influenced the homolysis process. These contaminants could not be conveniently removed (e.g., by ion exchange chromatography) because $(H_2O)_5CrC(CH_3)_2OH^{2+}$ would have undergone rapid acidolysis and homolysis. Nevertheless, the reproducibility of the kinetic data was excellent for a particular stock solution of Cr(II).

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Table III. Rate Coefficients and Activation Parameters for the Decomposition of $(H_2O)_5CrC(CH_3)_2OH^{2+}$ in Acidic Aqueous Solution[a]

parameter	temp, °C	acidolysis	homolysis	ref
k, s^{-1}	25.0	3.3×10^{-3}	0.13	3, 4
			0.21	this work
	15.0	1.45×10^{-3}		4
		1.33×10^{-3}		this work
ΔH^*, kJ mol^{-1}		72 ± 3	114 ± 1	3, 4
ΔS^*, J K^{-1} mol^{-1}		−46 ± 8	+120 ± 2	3, 4
ΔV^*, cm^3 mol^{-1}	15.0	+0.3 ± 0.2		this work
	25.0		+15.1 ± 1.6	this work

[a] Ionic strength = 1.0–1.1 M.

Table IV. Rate Coefficients k_{1A} for Acidolysis of $(H_2O)_5CrCH(CH_3)_2^{2+}$ at 0.1 MPa[a]

$[H^+]$, M	ionic strength,[b] M	temp, °C	10^4k_{1A}, s^{-1}
0.0997	1.0	15.38	0.294 ± 0.002
		20.14	0.624 ± 0.003
		25.22	1.10 ± 0.01
		30.04	1.93 ± 0.02
		35.06	3.31 ± 0.01
0.0997	0.22	25.04	1.14 ± 0.01

[a] Initial $[CrCH(CH_3)_2^{2+}] = 2 \times 10^{-3}$ M, $[Cr^{2+}] = 1 \times 10^{-2}$ M. [b] $HClO_4/LiClO_4$.

Table V. Pressure Dependence of k_{1A} for $(H_2O)_5CrCH(CH_3)_2^{2+}$ in Acidic, Aqueous Solution at 25 °C.

$[H^+]$, M	ionic strength, M	pressure, MPa	10^4k_{1A}, s^{-1}
0.0997	1.0	0.1	1.046 ± 0.002
		2.0	1.003 ± 0.012
0.0982	1.0	50.2	1.047 ± 0.003
		150.5	1.074 ± 0.003
		200.5	1.022 ± 0.003
		250.7	1.091 ± 0.002
		301.4	1.038 ± 0.004
0.0997	0.22	0.1	1.143 ± 0.005
		5.0	1.069 ± 0.001
		51.4	1.046 ± 0.001
		101.1	1.099 ± 0.002
		152.8	1.131 ± 0.001
		253.5	1.152 ± 0.001
		301.2	1.045 ± 0.002

Table VI. Rate Coefficients k_H for Homolysis of $(H_2O)_5CrCH(CH_3)_2^{2+}$ in Acidic Aqueous Solution[a]

$[H^+]$, M	ionic strength, M	temp, °C	10^4k_{obsd},[b] s^{-1}	10^4k_{1A}, s^{-1}
0.0982	1.0	15.04[c]	0.993 ± 0.010	0.693
		20.02[c]	2.00 ± 0.01	1.43
		25.06[c]	4.04 ± 0.09	
		25.05[d,e]	4.01 ± 0.03	
		25.04[c,e,f]	3.79 ± 0.02	2.95
0.0997		25.05[d]	3.99 ± 0.02	
		25.05[c]	4.19 ± 0.01	
0.0982		29.99[d]	8.17 ± 0.03	6.27
		34.98[d]	1.62 ± 0.02	12.8
0.0997		25.02[c]	3.73 ± 0.01	2.68
1.0[g]		25.02[d]	3.94 ± 0.02	2.89

[a] $(H,Li)ClO_4$, except as stated. [b] $k_{obsd} = k_{1A} + k_H$. [c] Scavenger was $Co(NH_3)_5Cl^{2+}$ (8×10^{-3} M). [d] Scavenger was Cu^{2+} (1×10^{-2} M). [e] $(H_2O_5)CrCH(CH_3)_2^{2+}$ purified by ion-exchange chromatography. [f] Exposure to spectrophotometer light beam limited to brief intervals for absorbance measurement. [g] CF_3SO_3H in place of $(H,Li)ClO_4$.

This complication did not show up in the acidolysis experiments where an excess of Cr(II) was employed. The pressure-dependence data are summarized in Table II. A plot of ln k_{obsd} vs. pressure was linear within the experimental uncertainties, and ΔV^* was calculated from this plot in the usual way.

A summary of the rate and activation parameters for the acidolysis and homolysis reactions of $(H_2O)_5CrC(CH_3)_2OH^{2+}$ is given in Table III.

Acidolysis of $(H_2O)_5CrCH(CH_3)_2^{2+}$. Presence of a four- to fivefold excess of Cr^{2+} over $(H_2O)_5CrCH(CH_3)_2^{2+}$ was sufficient to suppress homolysis completely. Plots of ln $(A_t - A_\infty)$ vs. t, where A_t and A_∞ are the optical absorbances measured at 400 nm at time t and after some 10 half-lives, respectively, were linear over at least 3 half-lives. In practice, better precision in the calculation of the corresponding rate coefficient k_{1A} was obtained by a non-linear least-squares regression analysis in which both k_{1A} and A_∞ were treated as parameters to be determined.

Tables IV and V summarize the acidolysis rate data as functions of temperature T and pressure P, respectively. Higher initial organochromium complex concentrations were necessary for the variable-pressure experiments to compensate for loss during the thermal re-equilibration of the assembly after pressurizing. Plots of ln (k_{1A}/T) vs. T^{-1}, and of ln k_{1A} vs. P, are linear within the experimental uncertainties, and the interpolated value of k_{1A} at 25.0 °C and 0.1 MPa (1.05×10^{-4} s^{-1}) is in exact agreement with that of Ryan and Espenson.[6] As with the $-C(CH_3)_2OH$ complex, k_{1A} is seen to be virtually independent of pressure. This applies equally at ionic strengths 1.0 M (with $LiClO_4$) and 0.22 M (no $LiClO_4$), although k_{1A} is typically 4–5% higher in the latter medium.

Homolysis of $(H_2O)_5CrCH(CH_3)_2^{2+}$. When a Cr^{2+} scavenger (Cu^{2+} or $Co(NH_3)_5Cl^{2+}$) was present in four- to fivefold excess over $(H_2O)_5CrCH(CH_3)_2^{2+}$, first-order decomposition kinetics (rate coefficient k_{obsd}) were observed over at least 3 half-lives so long as oxygen was rigorously excluded[6] and the scavenger was appropriately chosen. Experiments at temperatures above 25 °C required the addition of a small volume of concentrated scavenger solution to the thermally pre-equilibrated solution of hydroperoxide and Cr^{2+}; this was possible only with $Cu(ClO_4)_2$, as $[Co(NH_3)_5Cl](ClO_4)_2$ was insufficiently soluble. Low solubility also precluded use of the latter below 15 °C by any method. Copper(II) could not be used below 25 °C because the product $Cu^+(aq)$ disproportionated significantly over the longer reaction times; this process appeared to be accelerated photochemically, as copper metal deposited preferentially on those areas of the optical cell walls where the spectrophotometer light beam had passed. At 25 °C, however, both scavengers gave the same value of k_{obsd} ($=k_H + k_{1A}$).

These results are summarized in Table VI. The value of k_H obtained at 25 °C was significantly higher than that of Ryan and Espenson[6] ($k_H = (1.78 \pm 0.11) \times 10^{-4}$ s^{-1}), but it was accurately reproducible over a variety of conditions, including the use of different scavengers and sources of reagents and solvent water and, in some cases, prior purification of the organochromium complex by ion-exchange chromatography on Dowex 50W-X4 resin in the H^+ form. The discrepancy could not be explained, but we note that it amounts only to some 30% in k_{obsd}, the quantity actually measured, and this is not unusual between aqueous free-radical studies at different laboratories. The important point is that good reproducibility in the present experiments permitted reliable measurements of ΔH_H^* and of the pressure dependence of k_H.

Measurement of the effect of pressure on k_H for the 2-propyl complex necessitated slow reaction rates to allow time for full thermal equilibration of the pressure vessel, so that Cu^{2+} could not be used as the scavenger, and the ionic strength had to be lowered to 0.22 M to prevent precipitation of $[Co(NH_3)_5Cl](ClO_4)_2$ at the required concentration of 0.02 M. Values of k_H as a function of pressure are collected in Table VII.

Although the pressure dependence of ln k_H over the first 100 MPa might be adequately represented by a straight line of slope corresponding to $\Delta V_H^* \sim +24$ cm^3 mol^{-1}, the complete data set to 300 MPa makes it clear that ln k_H is actually a non-linear function of P (Figure 1) and that the low-pressure asymptote ΔV_0^* of ΔV_H^* is somewhat larger than +24 cm^3 mol^{-1}. A similar non-linearity could apply in the homolysis of $(H_2O)_5CrC$-

Table VII. Pressure Dependence of k_H for $(H_2O)_5CrCH(CH_3)_2^{2+}$ in Acidic, Aqueous Solution at 25 °C

$[H^+]$, M	ionic strength, M	pressure, MPa	10^4k_{obsd},[a] s^{-1}	10^4k_{1A},[c] s^{-1}	10^4k_H, s^{-1}
0.0997	1.0	0.1	4.00	1.05	2.95
	0.22	0.1	$3.73_4 \pm 0.006$		2.64 ± 0.05
		0.1[b]	$3.61_6 \pm 0.008$		2.52 ± 0.05
		1.5	$3.70_7 \pm 0.028$		2.61 ± 0.07
		24.9	$2.91_8 \pm 0.013$		1.82 ± 0.06
		50.1	$2.70_7 \pm 0.003$	1.10 ± 0.05	1.61 ± 0.05
		76.2	$2.29_0 \pm 0.003$		1.19 ± 0.05
		100.5	$2.07_0 \pm 0.005$		0.97 ± 0.05
		153.5	$1.89_6 \pm 0.002$		0.80 ± 0.05
		201.2	$1.70_0 \pm 0.008$		0.60 ± 0.05
		251.3	$1.57_8 \pm 0.002$		0.48 ± 0.05
		302.5	$1.45_1 \pm 0.009$		0.35 ± 0.05
		308.8	$1.49_8 \pm 0.014$		0.40 ± 0.06

[a] $k_{obsd} = k_{1A} + k_H$. [b] Run conducted in the pressure vessel. [c] Average of k_{1A} values from Table V.

$(CH_3)_2OH^{2+}$, but the pressure ceiling of the stopped-flow apparatus used in that study was 100 MPa and any curvature of the ln *k* vs. *P* plot would be obscured by the experimental uncertainty. Numerous functons to represent the curvature of a ln *k* vs. *P* plot have been proposed.[8] If, as the limited extent of the data set for the homolysis of $(H_2O)_5CrCH(CH_3)_2^{2+}$ dictates, one limits the number of parameters to three (including ln k_0, the value of ln k_H at zero applied pressure), the simple quadratic function 11 can

$$\ln k = \ln k_0 + BP + CP^2 \qquad (11)$$

be expected from experience to underestimate $\Delta V_0^* \ (= -BRT)$ slightly, while eq 12 and 13 may give better fits of the data than

$$\ln k = \ln k_0 + DP/(E + P) \qquad (12)$$

$$\ln k = \ln k_0 + F(e^{-GP} - 1) \qquad (13)$$

does eq 11 but generate large uncertainties in $\Delta V_0^* \ (= -DRT/E$ or $FGRT)$ because of the interdependence of the parameters. Equations 11–13 are empirical and have no mechanistic basis; if one assumes that curvature of the ln k_H vs. *P* plot is due entirely to a solvational change amounting to the gain of *x* molecules of water in the transition state and that the water solvating a cation is negligibly compressible relative to bulk water, combination of the modified Tait eq 14 for the compression of water (molar volume V_0 at 0.1 MPa)

$$(V_0 - V_p)/V_0 = \rho \ln (1 + P/\Pi) \qquad (14)$$

where $\Pi = 299.6$ MPa at 25 °C and $\rho = 0.1368$,[17] with eq 15 defining ΔV^*

$$(\partial \ln k/\partial P)_T = -\Delta V^*/RT \qquad (15)$$

gives eq 16, in which the curvature resides entirely in the final term, where *x* is the only unknown.[18,19]

$$\ln k = \ln k_0 - P\Delta V_0^*/RT - xV_0\rho\{(\Pi + P) \ln (1 + P/\Pi) - P\}/RT \qquad (16)$$

Blandamer et al.[20] have pointed out that curvature of a ln *k* vs. *P* plot could result if the initial dissociative step (rate coefficient k_1) of a decomposition reaction were followed by recombination (k_2) and onward (k_3) steps of comparable rates, i.e., if $\alpha = k_2/k_3$ were not far removed from unity, even though the corresponding volumes of activation ΔV_i^* (i = 1, 2, 3) for the individual steps might be independent of pressure. In the present case k_H for the homolysis step in reaction 8 was measured independently of k_{-H} and k_p, but probably it is itself a composite quantity, since homolysis of $(H_2O)_5Cr{-}R^{2+}$ will give initially fragments $(H_2O)_5Cr^{2+}$ and R· within the solvent cage, where they will recombine unless R· can escape to form an independent solute species.

$$CrR^{2+} \underset{k_2}{\overset{k_1}{\rightleftharpoons}} \{Cr^{2+}, R\cdot\} \xrightarrow{k_3} Cr^{2+} + R\cdot \xrightarrow{\text{scavenge}} \text{products} \qquad (17)$$

This leads to eq 18, in which the zero superscripts refer to atmospheric (in effect, zero) pressure.

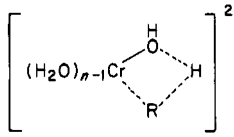
$$k_H = k_1/(1 + \alpha) = k_1^0 \exp(-P\Delta V_1^*/RT)/[1 + \alpha^0 \exp\{P(\Delta V_3^* - \Delta V_2^*)/RT\}] \qquad (18)$$

Equation 18 leads to the expectation that the apparent volume of activation for k_H could never decrease with increasing pressure, since α^0 is necessarily a positive number. For the homolysis of $(H_2O)_5CrCH(CH_3)_2^{2+}$, however, ΔV_H^* does decrease markedly with increasing pressure, and attempts to fit the data of Table VII to eq 18 succeed only if α^0 is allowed to become negative, which is physically meaningless. Thus, although the reaction 17 is quite likely realistic, it cannot in itself account for the pressure dependence of ΔV_H^*, which must originate in the intrinsic pressure dependence of at least one of ΔV_1^*, ΔV_2^*, or (most likely) ΔV_3^*, as discussed below.

The results of non-linear least-squares regression analyses of the data of Table VII according to eq 11–16 are summarized in Table VIII, which shows that eq 12 gives the best fit but that the other three-parameter equations are almost equally satisfactory, and ΔV_0^* may be taken to be +26 ± 2 $cm^3\ mol^{-1}$. The activation parameters for the decomposition of aqueous $(H_2O)_5CrCH(CH_3)_2^{2+}$ are summarized in Table IX.

Discussion

The acid-independent heterolysis of $(H_2O)_5CrR^{2+}$ will almost inevitably involve separation of RH rather than R^-, since the carbanion will be very basic while the aqua ligands are markedly acidic. Thus, the k_{1A} pathway, as well as the k_{2A} where observable, is appropriately called acidolysis. The very large deuterium isotope effect in acidolysis of $(H_2O)_5CrC(CH_3)_2OH^{2+}$ ($k_{1A}^H/k_{1A}^D = 6.3$), and its absence in homolysis, confirms this.[16] The transition state for the k_{1A} pathway can therefore be represented as



(19)

and would involve no *net* development of charge (though it may be quite polar) or major net changes in bond lengths. The observed volumes of activation of essentially zero for both R = $C(CH_3)_2OH$ and $CH(CH_3)_2$ are certainly consistent with these interpretation, although it is not clear whether the number *n* of coordinated water molecules in the transition state is 6 or 5, corresponding to associative and dissociative activation, respectively, or what its effect on ΔV_{1A}^* would be. Comparison with the ionogenic heterolysis of $(H_2O)_5CrI^{2+}$, for which aquation is apparently associatively activated with $\Delta V^* = -5.6$ $cm^3\ mol^{-1}$ and solvational changes are not large,[21] indicates that *n* is probably 6 in the transition states for heterolysis of these organochromium complexes, as seems to be typical of simple substitution reactions involving Cr(III) cations.[22]

The enthalpies and entropies of activation for acidolysis of $(H_2O)_5CrC(CH_3)_2OH^{2+}$ (Table III) and $(H_2O)_5CrCH(CH_3)_2^{2+}$ (Table IX) are typical of k_{1A} terms for decomposition of aqueous organochromium species.[2] The higher values of ΔH_{1A}^* and ΔS_{1A}^* for $(H_2O)_5CrCH(CH_3)_2^{2+}$ relative to $(H_2O)_5Cr(c\text{-}C_5H_9)^{2+}$ (73.5 kJ mol^{-1} and −62 J $K^{-1}\ mol^{-1}$, respectively)[23] and $(H_2O)_5CrC(CH_3)_2OH^{2+}$ may reflect the poorer solvation of the incipient R–H in the transition state, since the solubilities of RH in water are

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Table VIII. Analysis of the Pressure Dependence of k_H for the Homolysis of $(H_2O)_5CrCH(CH_3)_2^{2+}$ in Aqueous $HClO_4$[a]

	eq no.			
	11	12	13	16
$\ln (10^4 k_H{}^0)$	0.919 ± 0.037	0.941 ± 0.033	0.934 ± 0.034	0.926 ± 0.035
$B, D, F, \Delta V_0^*$	$-(9.77 \pm 0.71) \times 10^{-3}$	-4.04 ± 0.45	2.61 ± 0.24	25.6 ± 1.9
C, E, G, x	$(1.20 \pm 0.23) \times 10^{-5}$	347 ± 70	$(4.18 \pm 0.70) \times 10^{-3}$	-10.8 ± 1.9
10^3(mean sq error)	5.26	3.76	4.19	4.61
ΔV_0^*, $cm^3\ mol^{-1}$	$+24.2 \pm 1.8$	$+28.9 \pm 9.0$	$+27.0 \pm 7.0$	$+25.6 \pm 1.9$

[a] Ionic strength = 0.22 M, 25 °C.

Table IX. Rate Coefficients and Activation Parameters for the Decomposition of $(H_2O)_5CrCH(CH_3)_2^{2+}$ in Acidic Aqueous Solution at 25 °C[a]

parameter	acidolysis	homolysis
k, s^{-1}	1.05×10^{-4} [b]	1.78×10^{-4} [b]
	1.05×10^{-4}	3.04×10^{-4}
	1.10×10^{-4} [c]	2.61×10^{-4} [c]
ΔH^*, kJ mol^{-1}	87.0 ± 2.9	105.7 ± 1.3
ΔS^*, J K^{-1} mol^{-1}	-29.2 ± 9.8	42.3 ± 4.5
ΔV^*, $cm^3\ mol^{-1}$	-0.2 ± 0.2	
	0.0 ± 0.4 [c]	26 ± 2 [c]

[a] Ionic strength = 1.0 and $[H^+]$ = 0.1 M, except as indicated. [b] Reference 6. [c] Ionic strength = 0.22 M.

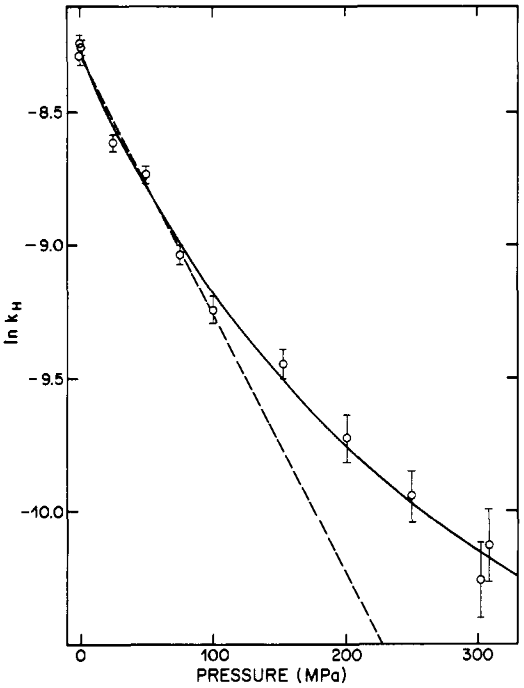


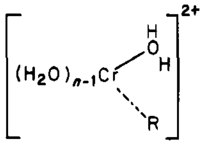
Figure 1. Pressure dependence of ln k_H for the homolysis of $(H_2O)_5CrCH(CH_3)_2^{2+}$ at 25.0 °C and ionic strength 0.22 M. Solid line: least-squares fit according to eq 12. Broken line: linear least-squares fit of data up to 100.5 MPa, corresponding to $\Delta V_H^* = +24._3$ $cm^3\ mol^{-1}$.

propane ≪ cyclopentane ≪ 2-propanol, but the *similarities* are more significant than the differences.

In particular, ΔH_{1A}^* and ΔS_{1A}^* for these acidolyses are all much smaller than the corresponding quantities for homolysis, as is generally the case.[2] For the homolysis of $(H_2O)_5CrCH(CH_3)_2^{2+}$, k_H is some 400-fold smaller than for $(H_2O)_5CrC(CH_3)_2OH^{2+}$, largely because of the less favorable ΔS_H^*, and the 2-propyl complex seems to behave more like the cyclopentyl analogue, for which $k_H{}^{298} = 1.1 \times 10^{-4}$ s^{-1} although $\Delta H_H^* = 126$ kJ mol^{-1} and $\Delta S_H^* = +103$ J K^{-1}.[23] No simple rationale is evident that would encompass k_H, ΔH_H^*, and ΔS_H^* for the $-CH(CH_3)_2$, $-C(CH_3)_2OH$, and $-c-C_5H_9$ complexes, probably because these are, in all likelihood, composite quantities (eq 17).

The volumes of activation ΔV_H^* for homolysis of both $(H_2O)_5CrC(CH_3)_2OH^{2+}$ and $(H_2O)_5CrCH(CH_3)_2^{2+}$ are strongly positive and, in the latter case at least, pressure dependent. One expects Cr–C bond homolysis per se to make a positive contribution to ΔV_H^*, but the work of Neuman[24] on C–C homolysis indicates that this is unlikely to amount to more than +4 cm^3 mol^{-1}, and less if the transition state is appreciably polar. This contribution, however, refers only to step k_1 in reaction 17. Neuman[24] points out that the intracage recombination path k_2 will be favored by high pressure, so making the overall ΔV_H^* more positive. In addition, the step k_3, which leads to observable reaction, requires the partial breakup of the solvent cage as well as the outward movement of R·, so that *desolvation* of $(H_2O)_5CrR^{2+}$ is likely to be a major contributor to ΔV_H^*.

This would explain the curvature of the ln k_H vs. pressure plot for $(H_2O)_5CrCH(CH_3)_2^{2+}$; on the basis of eq 16, some 10–11 waters of solvation are thrust aside in step k_3. It has been argued elsewhere[19] that water in the outer coordination spheres of a trivalent cation has an average molar volume about 2.4 cm^3 mol^{-1} smaller than that of bulk water; thus, the intrinsic (i.e., nonsolvational) part of ΔV_H^* is probably close to zero—that is, essentially identical with ΔV_{1A}^* for the corresponding acidolysis reaction. This is indeed quite feasible; the transition state of the homolytic step k_1 in reaction 17



(20)

differs significantly from that for heterolysis only in the distribution of some electrons and a proton, and hence the molar volumes of the isomeric transition states will be closely similar. In heterolysis, however, the resulting assemblage $\{(H_2O)_{n-1}CrOH^{2+}, RH\}$ cannot recombine, and the separation of RH makes no further contribution to the kinetic parameters, including ΔV_{1A}^*; in homolysis, net reaction can only be observed if step k_3, with its major volume effects, is completed. Significantly, *both* the enthalpies *and* the entropies of activation for these homolyses are larger (more positive) than those for the corresponding acidolyses, as is characteristic of processes that differ mainly in solvation.[22]

The strongly positive ΔV_H^* value (+15 cm^3 mol^{-1}) for the homolysis of $(H_2O)_5CrC(CH_3)_2OH^{2+}$ may be similarly interpreted, although information on the possible pressure dependence of ΔV_H^* is lacking, for technical reasons, and the asymptotic ΔV_0^* at zero pressure could be as much as 17 cm^3 mol^{-1}. In any event, ΔV_0^* for the homolysis of the 2-propyl complex (26 cm^3 mol^{-1}) is somewhat larger, which is in accordance with the poorer solvation of R· = ·$CH(CH_3)_2$ relative to ·$C(CH_3)_2OH$ expected on the basis of the solubilities of RH in water.

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Registry No. $(H_2O)_5CrC(CH_3)_2OH^{2+}$, 32108-93-3; $(H_2O)_5CrCH(CH_3)_2$, 60764-48-9; 2,3-dimethyl-2-butyl hydroperoxide, 28888-35-9; 2,3-dimethyl-2-butanol, 594-60-5.

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