Anion-Catalyzed Heterolysis of Chromium–Carbon σ Bonds. Effect of Different Anions, Temperature, and Pressure

Wolfgang Gaede,[1a] Rudi van Eldik,*,[1a] Haim Cohen,[1b,c] and Dan Meyerstein*,[1b]

Institute for Inorganic Chemistry, University of Witten/Herdecke, Stockumer Strasse 10, 5810 Witten, Germany, R. Bloch Coal Research Center and Chemistry Department, Ben Gurion University of the Negev, Beer-Sheva, Israel, and Nuclear Research Center Negev, Beer-Sheva, Israel

The anion-catalyzed heterolysis reaction of $(H_2O)_5CrC(CH_3)_2OH^{2+}$ was studied as a function of anion concentration, temperature, and pressure for a series of 10 different organic and inorganic oxy anions, for which the pK_a values range between 0 and 7. The reported rate data indicate that the catalytic effect increases with basicity of the anion. The volumes of activation for the catalyzed heterolysis reactions are all significantly positive and support the operation of a dissociatively activated heterolysis mechanism. The results are discussed in reference to related data reported in the literature.
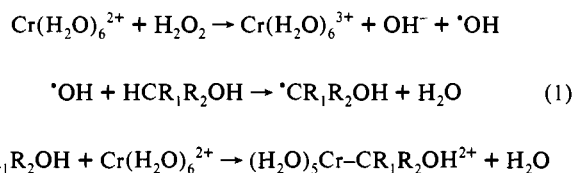
Introduction

We recently reported a detailed study of the effect of the nonparticipating ligands, temperature, and pressure on the acetate-catalyzed heterolysis of (α-hydroxyalkyl)chromium(III) complexes,[2] following earlier ambient-temperature and -pressure studies reported on the same topic in the literature.[3–7] The results of our study clearly demonstrated that the catalytic effect resulted from a trans-labilization effect by coordinated acetate and, on the basis of the positive volumes of activation, induced the operation of a dissociatively activated heterolysis mechanism. Furthermore, it was shown that the metal–carbon bond in such systems drastically accelerates ligand substitution reactions in the trans position,[2,4] such that acetate rapidly enters the coordination sphere of the (α-hydroxyalkyl)chromium(III) complex to catalyze the subsequent slower heterolysis reaction. In order to gain more insight into the intimate nature of the trans labilization of the chromium–carbon heterolysis reaction, and the possibility that similar reactions may account for important catalytic cleavage of metal–carbon bonds in biological systems, we have now undertaken a systematic study of the effect of different anions on heterolysis reactions of chromium–carbon bonded complexes. In addition, the temperature and pressure dependence of the catalyzed reactions was also studied in order to reveal more mechanistic details.

Experimental Section

Materials. Chromium(II) solutions were prepared by dissolving chromium metal powder (BDH) in 1 M $HClO_4$ (3 g of Cr in 150 mL of 1 M $HClO_4$) under Ar atmosphere for 12 h. The Ar was purified from traces of O_2 by passing it through a washbottle containing a 0.5 M Cr(II) solution. Deionized Millipore water was used to prepare all solutions, and all other chemicals were of analytical reagent grade. Solutions were prepared in syringes and deaerated by passing Ar through them for 15 min. Mixing and dilution of the solutions were accomplished with a syringe technique,[8] and small glass disks in the syringes were used to mix the solutions. The ionic strength was adjusted with $NaClO_4$ (Merck).

Measurements. The Cr(II) concentration was determined spectrophotometrically by following the reduction of $Co(NH_3)_5Cl^{2+}$ at 532 nm ($\epsilon = 49.6$ M^{-1} cm^{-1}) and 362 nm ($\epsilon = 48.1$ M^{-1} cm^{-1}).[9] UV–vis spectra were recorded on Varian Cary 1 and Shimadzu UV-250 spectrophotometers. The pH of the test solutions was measured using a Metrohm 632 instrument under Ar atmosphere. Ambient-pressure kinetic measurements were performed on a Durrum D110 stopped-flow instrument, whereas experiments at elevated pressure were performed on a homemade high-pressure stopped-flow unit capable to go to 200 MPa.[10] Both instruments were thermostatated to ±0.1 °C. Data acquisition and handling were performed on on-line computer systems using the OLIS KINFIT set of programs.[11]

Production of Organochromium Complexes. The organochromium(III) complexes were prepared in situ via the modified Fenton reaction. In this procedure a Cr(II) solution containing an alcohol is mixed with a H_2O_2 solution. Under these conditions the sequence of reactions in (1)

$$Cr(H_2O)_6^{2+} + H_2O_2 \rightarrow Cr(H_2O)_6^{3+} + OH^- + {}^\bullet OH$$

$$^\bullet OH + HCR_1R_2OH \rightarrow {}^\bullet CR_1R_2OH + H_2O \qquad (1)$$

$$^\bullet CR_1R_2OH + Cr(H_2O)_6^{2+} \rightarrow (H_2O)_5Cr\text{–}CR_1R_2OH^{2+} + H_2O$$

occurs.[5,6] To study the influence of different anions on the heterolysis of the (α-hydroxyalkyl)chromium(III) complex, these were added to the Cr(II) solution prior to mixing with H_2O_2. The rate constant for the reaction of ${}^\bullet OH$ with alcohols is $>5 \times 10^7$ M^{-1} s^{-1},[12] whereas the reaction of ${}^\bullet OH$ with the investigated anions is significantly slower[12] and does not interfere under the selected experimental conditions. Throughout this study $[Cr(II)] \geq 2 \times 10^{-3}$ and $[H_2O_2] \geq 2 \times 10^{-4}$ M, with Cr(II) in at least a 10-fold excess. Since the rate constant for the first step in reaction 1 is $\geq 6 \times 10^4$ M^{-1} s^{-1}, the formation of the organochromium complex terminates in less than 40 ms after mixing the H_2O_2 and chromous/alcohol solutions. It follows that any heterolysis reaction with half-life longer than ca. 50 ms can be studied using this procedure.

Results and Discussion

Studies at 25 °C and Ambient Pressure. The organochromium(III) species produced in (1) is unstable and decomposes depending on the reaction conditions along various routes. The spontaneous homolysis reaction, i.e. the reverse reaction of the last step in (1), can be suppressed by using an excess of

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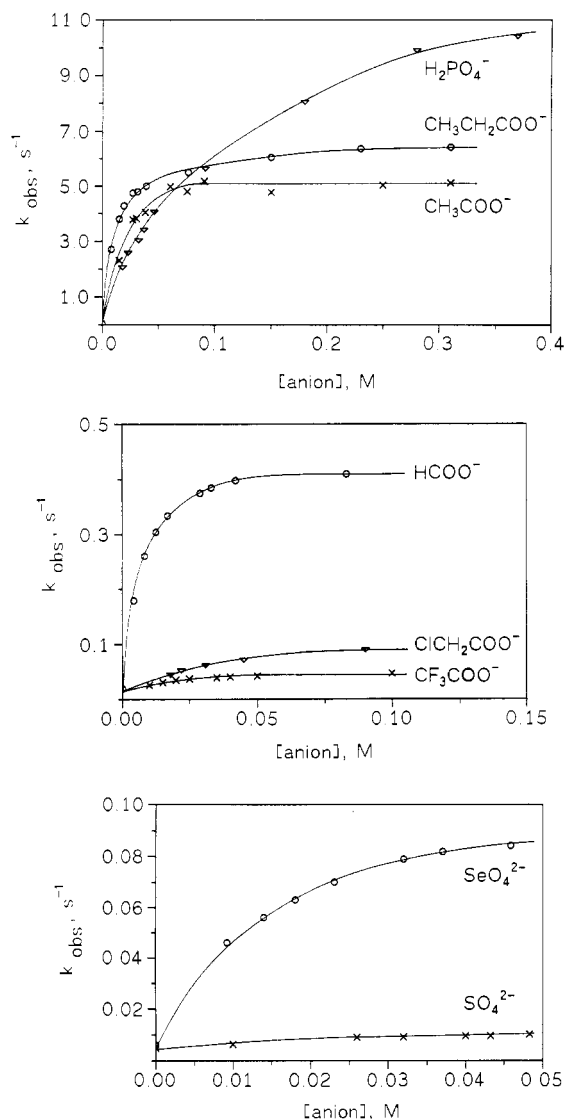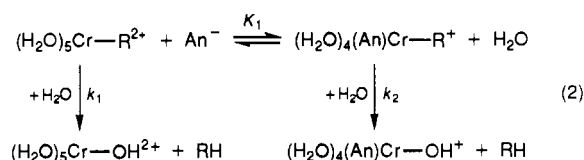
Figure 1. Plots of k_{obs} versus [anion] for the heterolysis of $(H_2O)_4(An)Cr-R^+$: (a, top) CH_3COO^-, $CH_3CH_2COO^-$, $H_2PO_4^-$; (b, middle) CF_3COO^-, $ClCH_2COO^-$, $HCOO^-$; (c, bottom) SO_4^{2-}, SeO_4^{2-}. Experimental conditions: $[Cr(II)] = 3 \times 10^{-3}$ M; $[H_2O_2] = 3 \times 10^{-4}$ M; $[i\text{-PrOH}] = 0.5-1.0$ M; $\mu = 0.5$ M; for pH see Table I.

$Cr(H_2O)_6^{2+}$.[6] The heterolysis reaction of the (α-hydroxyalkyl)chromium(III) complex $(H_2O)_5Cr-R^{2+}$, where R = C-$(CH_3)_2OH$, was studied using the stopped-flow technique described above, in the presence of a series of anions. The solutions contained 3×10^{-3} M Cr(II), 3×10^{-4} M H_2O_2, 0.5–1.0 M 2-propanol or methanol, and $NaClO_4$ to maintain 0.5 M ionic strength. The hererolysis reactions were studied at 321 nm, where they exhibited excellent first-order behavior under the selected conditions. The effect of the different anions on the value of the first-order rate constant, k_{obs}, is reported in Figure 1a–c in the form of plots of k_{obs} versus [anion], where all the cited concentrations are those of the deprotonated, anionic species. During such experiments the pH was kept constant, since this will control the concentration of the anionic species. Earlier work[4] has clearly shown that the increase in k_{obs} on increasing the pH could be accounted for in terms of the increase in the concentration of the anions. The pH for each series of measurements was selected above the pK_a value of the corresponding acid to ensure that a large fraction of the acid is present in the anionic form and that sufficient buffer capacity exists. In all cases the heterolysis is accelerated to a smaller or larger extent by the presence of the anions, and k_{obs} reaches a limiting value at high anion concentrations. The small intercepts in these plots represent the

spontaneous, uncatalyzed heterolysis reaction, which is in most cases negligible in comparison to the contribution of the catalyzed reaction path. The plots in Figure 1a–c indicate that $H_2PO_4^-$, $CH_3CH_2COO^-$, and CH_3COO^- are the most effective anionic catalysts.

In all cases the saturation of k_{obs} with increasing anion concentration is assigned to the formation of a 1:1 complex of $(H_2O)_5Cr-R^{2+}$ with an anion (An^-) to produce a more reactive $(H_2O)_4(An)Cr-R^+$ species as outlined in the general scheme in (2).[2-6] It could be shown[2] that the reactions of the anions with

$$(H_2O)_5Cr-R^{2+} + An^- \underset{}{\overset{K_1}{\rightleftharpoons}} (H_2O)_4(An)Cr-R^+ + H_2O$$

$$+H_2O \downarrow k_1 \qquad\qquad\qquad +H_2O \downarrow k_2 \qquad\qquad (2)$$

$$(H_2O)_5Cr-OH^{2+} + RH \qquad (H_2O)_4(An)Cr-OH^+ + RH$$

the $Cr-R^{2+}$ species are too fast for stopped-flow experiments. The anion must react with the metal center in the trans position due to the strong trans-labilizing effect of the metal–carbon σ bond. It should be noted that under the selected conditions only the acid-independent heterolysis path is observed. The kinetic data were fitted with a nonlinear regression program to the rate expression (3) by using the k_1 values given in Table I, which

$$k_{obs} = \frac{k_1 + k_2 K_1[An^-]}{1 + K_1[An^-]} \qquad (3)$$

resulted in excellent regression coefficients. The results are summarized in Table I, from which it follows that most anions coordinate effectively to $(H_2O)_5Cr-R^{2+}$. The observed correlation between the kinetic data for the catalytic pathway and the pK_a value of the acidic form of the anionic species will be discussed later on.

The glycolate-catalyzed heterolysis reaction exhibits a peculiar dependence of k_{obs} on the glycolate concentration as shown for two different pH values in Figure 2. By way of comparison the closely related lactate-catalyzed reaction exhibits a quite normal dependence of k_{obs} on the lactate concentration. The maxima in the glycolate rate plots suggest that more than one catalytic species is produced as a function of glycolate concentration. UV–vis spectra recorded for Cr(II) solutions in the presence of glycolate indicate an absorbance increase at 428 nm with increasing glycolate concentration up to 0.043 M, although the effect is rather small. One possibility is that glycolate may coordinate to Cr(II) as a chelate, involving the OH group at low glycolate concentrations, which may cause an additional labilization effect and account for the maxima in the plots in Figure 2. Such chelate formation is only expected to occur at a relatively low glycolate concentration, since at higher concentrations ring closure will have to compete with substitution by a second glycolate anion. In the case of oxalate such chelation reactions were found to be rather slow,[13] thus making the competition with a second entering nucleophile quite realistic. However, in the present case all reactions prior to heterolysis must be fast since a similar result was observed when glycolate is added to the reaction mixture after formation of $(H_2O)_5Cr-C(CH_3)_2OH^{2+}$.[2,7] A similar effect does not occur in the case of lactate (Figure 2), even at higher pH, which could mean that the suggested chelation of glycolate is prevented by the additional methyl group in lactate. Another possible explanation may involve the formation of a glycolate-bridged complex involving two $Cr-R^{2+}$ moieties at low glycolate concentration and involving both the carboxylate and hydroxy binding sites. Once again higher glycolate concentrations will favor the formation of the carboxylate-bound glycolate species. The formation of such a bridged species is also in line with the

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Table I. Rate and Equilibrium Constants for the Spontaneous and Anion-Catalyzed Heterolysis of Chromium–Carbon σ Bonds at 25 °C[a]

anion	pK_a	pH	$k_1,^d s^{-1}$	k_2, s^{-1}	K_1, M^{-1}	$k_2K_1,^e M^{-1} s^{-1}$
CF_3COO^-	<0	3.0	6×10^{-3}	0.05 ± 0.01	80 ± 8	3.7 ± 0.9
$SO_4^{2-\ b}$	1.9	3.0	6×10^{-3}	0.07 ± 0.01	62 ± 2	4.5 ± 0.8
$SeO_4^{2-\ b}$	1.9	3.0	6×10^{-3}	0.11 ± 0.01	59 ± 2	6.5 ± 0.8
$ClCH_2COO^{-\ b}$	2.85	3.8	1×10^{-2}	0.12 ± 0.01	25 ± 1	3.1 ± 0.4
$CH_3CH(OH)COO^{-\ c}$	3.08	3.5	8×10^{-3}	0.06 ± 0.01	69 ± 4	4.5 ± 0.6
$HCOO^{-\ c}$	3.7	4.5	1.7×10^{-2}	0.44 ± 0.04	151 ± 5	66.7 ± 0.8
$HOCH_2COO^{-\ c}$	3.8	4.5	1.7×10^{-2}	0.45 ± 0.02	84 ± 4	83.0 ± 0.8
$HOCH_2COO^-/L15^c$	3.8	4.5	3×10^{-2}	0.16 ± 0.02	461 ± 20	73.8 ± 0.8
$CH_3COO^{-\ b}$	4.75	5.3[f]	2.6×10^{-2}	6.8 ± 0.3	41 ± 2	277 ± 24
$CH_3CH_2COO^{-\ b}$	4.9	5.4[f]	2.7×10^{-2}	6.5 ± 0.4	91 ± 2	593 ± 27
$H_2PO_4^-/H_2PO_4^{2-\ b}$	2.1/7.2[g]	3.2	7×10^{-3}	13.5 ± 0.6	8.8 ± 0.7	119 ± 13

[a] Experimental conditions: $[Cr(II)] = 3 \times 10^{-3}$ M; $[H_2O_2] = 3 \times 10^{-4}$ M; $\mu = 0.5$ M. [b] $[i\text{-PrOH}] = 0.5$ M. [c] $[i\text{-PrOH}] = 1.0$ M. [d] Evidence for hydroxide-assisted heterolysis at pH > 3.0 has been reported[5] and can account for the pH dependence of k_1. The contribution of this step, however, remains negligible in the presence of anion catalysis. [e] From fit of data. [f] No precipitation of chromium hydroxide occurs under these conditions due to the presence of the carboxylate ions. [g] Expected pK_a value of coordinated $H_2PO_4^-$ will cause partial deprotonation to HPO_4^{2-}: see Discussion.
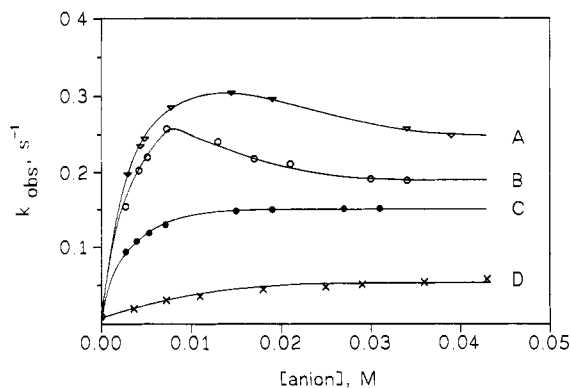

Figure 2. Plots of k_{obs} versus [anion] for the heterolysis of $(H_2O)_4(An)Cr–R^+$ with $An^- = CH_3CH(OH)COO^-$ and $HOCH_2COO^-$ at two different pH values. Experimental conditions: $[Cr^{2+}] = 3 \times 10^{-3}$ M; $[H_2O_2] = 3 \times 10^{-4}$ M; $[i\text{-PrOH}] = 1.0$ M; $\mu = 0.5$ M. Key: (A) heterolysis with $HOCH_2COO^-$ at pH = 5.3; (B) heterolysis with $HOCH_2COO^-$ at pH = 4.6; (C) heterolysis of $([15]aneN_4)(An)Cr–R^+$ for $An^- = HOCH_2COO^-$ at pH = 4.5; (D) heterolysis with $CH_3CH(OH)COO^-$ at pH = 3.5.
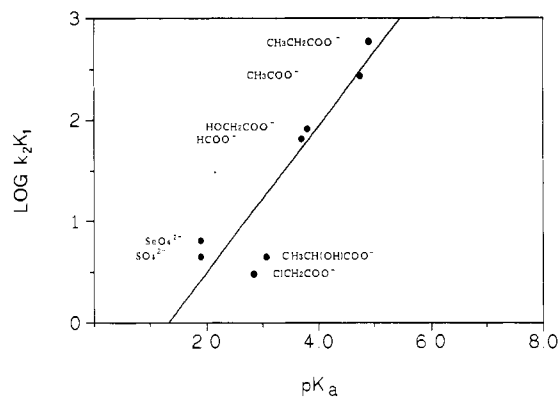

Figure 3. Plot of log k_2K_1 versus pK_a for data in Table I.

very similar limiting rate constant found when [15]aneN₄ is used to complex Cr(II) (see Figure 2) but is not in agreement with the totally different concentration dependence observed in the latter case. Thus it seems more likely that chelation instead of bridge formation can account for the peculiar concentration dependence found for glycolate. An increase in pH would make the bridge formation more effective and could cause the maximum in the plot to move to higher glycolate concentration (Figure 2).

The values of k_2K_1 and k_2 in Table I exhibit some correlation with the pK_a value of the corresponding protonated form of the anions responsible for the catalytic effect, in that the rate of the catalyzed heterolysis reaction increases with increasing pK_a value (Figures 3 and 4). Thus with increasing basicity, more electron density from the anion is shifted onto the metal center and will cause a labilization of the Cr–R bond. There are significant
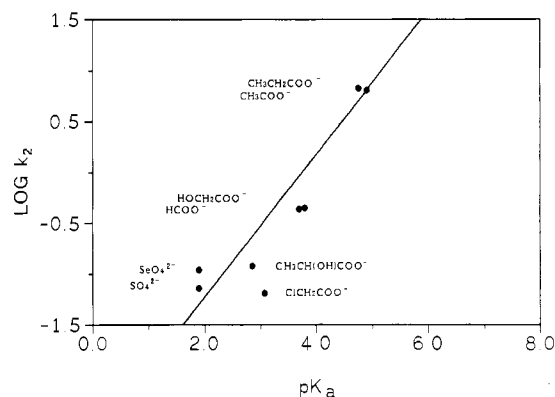

Figure 4. Plot of log k_2 versus pK_a for data in Table I.

differences between the data for inorganic and organic ligands, which may be related to the type of bonding with the metal center, which can be expected to be stronger in the case of the inorganic ligands. The data for $H_2PO_4^-/HPO_4^{2-}$ do not fit the general correlation found for the other anions when the corresponding pK_a values for H_3PO_4 and $H_2PO_4^-$ are used. In this respect it should be kept in mind that coordinated $H_2PO_4^-$ will have a significantly lower pK_a value than uncoordinated $H_2PO_4^-$. In fact, in an earlier study[14] of a Ni(III) hexamethylcyclam complex, coordinated $H_2PO_4^-$ was shown to have a pK_a value of 3.8 ± 0.2, i.e. more than 3 units lower than for uncoordinated $H_2PO_4^-$. This means that the coordinated anion in the case of the Cr(III) system may be a mixture of $H_2PO_4^-$ and HPO_4^{2-}, which makes the assignment of an appropriate pK_a value difficult. The general trend observed in Figures 3 and 4 indicates that the donor ability of the coordinated anion most probably causes a trans-labilization effect similar to that suggested to account for the catalytic effect of acetate.[2-5]

The value of K_1 is smaller than expected for $ClCH_2COO^-$ since the value for CF_3COO^- is significantly larger. Electron-withdrawing properties of the substituents will weaken the bond to the Cr(III) center but should then reverse the order of the K_1 values referred to. Other anions that did not reveal a significant catalytic effect are F^-, Cl_2CHCOO^-, and Cl_3CCOO^-. These all have low basicity and weak coordination ability and are not capable to coordinate effectively to the $Cr–R^{2+}$ species. In addition, chelate ligands such as oxalate and malonate did not result in clean first-order heterolysis reactions, as mentioned above, and was therefore not further investigated.

Studies at Different Temperatures and Pressures. From the anion concentration dependences of k_{obs} reported in Figure 1a–c, appropriate conditions were selected to study the temperature and pressure dependences of k_2K_1 and k_2 as done for acetate

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Table II. Rate and Activation Parameters for the Heterolysis of (α-Hydroxyalkyl)chromium(III) in the Presence of Different Anions

anion	[An⁻], M	k_{obs} at 25 °C, s⁻¹	ΔH^*, kJ mol⁻¹	ΔS^*, J K⁻¹ mol⁻¹
CF_3COO^- [a]	0.01	0.026	64 ± 3	−60 ± 9
	0.1	0.047	38 ± 2	−143 ± 8
SO_4^{2-} [b]	0.02	0.033	67 ± 3	−48 ± 10
$ClCH_2COO^-$ [b]	0.018	0.044	63 ± 2	−58 ± 7
	0.27	0.114	57 ± 11	−71 ± 36
$CH_3CH(OH)COO^-$ [a]	0.0036	0.02	57 ± 3	−84 ± 12
	0.036	0.054	47 ± 2	−112 ± 7
$HCOO^-$ [a]	0.0083	0.26	65 ± 6	−388 ± 18
	0.083	0.41	61 ± 3	−48 ± 11
$HOCH_2COO^-$ [a]	0.0034	0.096	56 ± 2	−78 ± 8
	0.034	0.189	45 ± 4	−109 ± 15
CH_3COO^- [b]	0.015	3.4	67 ± 3	−10 ± 10
	0.31	5.4	61 ± 2	−25 ± 4
$CH_3CH_2COO^-$ [b]	0.019	4.28	63 ± 2	−21 ± 7
	0.31	6.43	40 ± 3	−95 ± 10
$H_2PO_4^-$ [c]	0.014	2.0	45 ± 3	−88 ± 9
	0.37	10.4	34 ± 1	−111 ± 4

[a] [i-PrOH] = 1 M. [b] [i-PrOH] = 0.5 M. [c] [i-PrOH] = 0.25 M. $[Cr(II)]_T$ = 3 × 10⁻³ M, $[H_2O_2]$ = 3 × 10⁻⁴ M, μ = 0.5 M.

Table III. Volumes of Activation for the Heterolysis of (α-Hydroxylalkyl)chromium(III) with Different Anions at 25 °C[a]

anion	[anion], M	pH	[i-PrOH], M	ΔV^*, cm³ mol⁻¹
CF_3COO^-	0.01	3.0	1.0	+14.2 ± 0.4
	0.1	3.0	1.0	+12.1 ± 0.7
SO_4^{2-}	0.026	3.0	0.5 (MeOH)	+11.2 ± 0.4
	0.25	3.0	0.5 (MeOH)	+10.5 ± 0.8
$ClCH_2COO^-$	0.018	3.8	0.5	+19.5 ± 1.1
	0.27	3.8	0.5	+7.4 ± 0.4
$CH_3CH(OH)COO^-$	0.0042	3.5	1.0	+9.1 ± 0.3
	0.036	3.5	1.0	+8.5 ± 0.1
$HCOO^-$	0.0083	4.5	1.0	+10.8 ± 0.3
	0.042	4.5	1.0	+7.8 ± 0.4
$HOCH_2COO^-$	0.0039	4.5	1.0	+13.5 ± 0.5
	0.03	4.5	1.0	+8.0 ± 0.3
CH_3COO^-	0.015	5.3	0.5	+15.1 ± 0.8
	0.31	5.3	0.5	+11.3 ± 0.6
$CH_3CH_2COO^-$	0.015	5.4	0.5	+14.1 ± 0.6
	0.31	5.4	0.5	+10.1 ± 0.8
$H_2PO_4^-$	0.018	3.2	0.5	+15.5 ± 0.3
	0.37	3.2	0.5	+11.7 ± 1.2

[a] Experimental conditions: [Cr(II)] = 3 × 10⁻³ M, $[H_2O_2]$ = 3 × 10⁻⁴ M, μ = 0.5 M.

before.[2] The results in Table II summarize the thermal activation parameters measured at low and high anion concentrations, i.e. to distinguish between the contributions of k_2 and K_1. In general, ΔH^* decreases with increasing anion concentration, which demonstrates that $\Delta H^°(K_1)$ is significantly positive, since this term contributes at low anion concentration. In a similar way, ΔS^* becomes more negative at higher anion concentration, demonstrating a positive contribution from $\Delta S^°(K_1)$. The values of ΔS^* for k_2 are all significantly negative and demonstrate that heterolysis of the Cr–R bond involves significant bond formation presumably with a solvent molecule.[2]

The ΔV^* data summarized in Table III exhibit some interesting and consistent trends. In most cases ΔV^* decreases with increasing anion concentration and remains significantly positive under all conditions. At low anion concentration $\Delta V^*(k_2K_1) = \Delta V^*(k_2) + \Delta \bar{V}(K_1)$, from which it follows that $\Delta \bar{V}(K_1)$ can be estimated from the difference $\Delta V^*(k_2K_1) - \Delta V^*(k_2)$, i.e. the volume of activation measured at low and high anion concentrations, respectively. It follows that $\Delta \bar{V}(K_1)$ = 3–7 cm³ mol⁻¹, fairly independent of the nature of the anion, and represents the reaction volume for the substitution of a water molecule by an anion. This process is accompanied by charge neutralization and an overall volume increase of a few cm³ mol⁻¹. The values of $\Delta V^*(k_2)$ measured at high anion concentrations are in most cases

significantly positive, ca. 10 cm³ mol⁻¹, and support a dissociatively activated heterolysis reaction for the catalyzed process. This must be correlated to the trans-labilization effect of the coordinated anions, in which their basicity accounts for the degee of labilization, i.e. the value of k_2K_1. The nature of the mechanism can probably be best described as dissociative interchange (I_d) during which the breakage of the chromium–carbon σ bond is accompanied by bond formation with the entering solvent molecule. By way of comparison, the volume of activation for the spontaneous heterolysis reaction was found to be close to zero[15] and interpreted in terms of attack of a solvent molecule on the Cr–R bond during which RH is separated and OH⁻ binds to the metal center. The significantly more positive $\Delta V^*(k_2)$ values reported in Table III therefore underline the importance of a dissociatively activated heterolysis process.

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