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Kinetics and Mechanism of the Acetate-Catalyzed Heterolysis of the Metal–Carbon σ Bond of (α-Hydroxyalkyl)chromium(III) Complexes. Effects of Nonparticipating Ligands, Temperature, and Pressure

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The acetate-catalyzed heterolysis reaction of two (α-hydroxyalkyl)chromium(III) complexes, Cr^{III}–CH_2OH and Cr^{III}–$C(CH_3)_2OH$, with three types of nonparticipating ligands $(H_2O)_5Cr$–R^{2+}, *trans*-([15]aneN_4)(H_2O)Cr–R^{2+}, and *cis*-(nta)(H_2O)Cr–R^-, has been studied as a function of acetate concentration, temperature, and pressure. The reported rate and activation parameters demonstrate that the catalytic effect results from a trans-labilization effect by coordinated acetate and involves the attack by a solvent water molecule on the metal–carbon bond. The positive volumes of activation support the operation of a dissociatively activated heterolysis mechanism, which is in line with the suggested labilization effect by coordinated acetate.

Introduction

Divalent chromium complexes react readily with a variety of aliphatic free radicals to form relatively stable complexes with chromium–carbon σ bonds.[2,3] Many of these complexes decompose, in the presence of excess chromium ions in aqueous solutions, via the heterolytic cleavage of the chromium–carbon bond, reaction 1, to yield as the final stable products tervalent chromium

$$LCr\text{–}R^{2+} + H_2O \xrightarrow{H^+} LCr\text{–}OH_2^{3+} + RH \qquad (1)$$

and the corresponding organic product. The rate of decomposition obeys the rate law (2), in which k_1 represents the spontaneous

$$-d[LCr\text{–}R^{2+}]/dt = \{k_1 + k_2[H^+]\}[LCr\text{–}R^{2+}] \qquad (2)$$

and k_2 the acid-catalyzed reaction paths, respectively.[4] Earlier investigations[5,6a] of the heterolysis reaction for different α-hydroxyalkyls (R) and nonparticipating ligands (L) demonstrated that the presence or absence of a cis-aqua ligand in $(H_2O)_5Cr$–R^{2+}, *cis*-(nta)(H_2O)Cr–R^-, *trans*-([15]aneN_4)(H_2O)Cr–R^{2+}, and (edta)Cr–R^{2-} has a negligible effect on the specific rate of the heterolysis process. This observation was interpreted as suggesting that an electrophilic attack of a solvent water molecule at the carbon center of the chromium–carbon σ bond is the rate-determining step in the heterolysis process.

Of particular interest is the observed enhancement of the heterolysis reaction in the presence of acetate.[5–7] Ogino and coworkers[7] found that addition of acetate to a solution of $(H_2O)_5CrCH_2OH^{2+}$ causes a remarkable acceleration of the rate of the heterolysis reaction. They interpreted their kinetic data in terms of a rapid formation of $(H_2O)_4(Ac)CrCH_2OH^+$ (formation constant of 11 ± 1 M^{-1} at 25 °C) followed by an acetate-induced heterolysis reaction of this complex, which was found to be 1600 times faster than the heterolysis of $(H_2O)_5CrCH_2OH^{2+}$. Meyerstein and co-workers[5,6] reported similar observations and in addition studied the acetate effect in the presence of two chelating ligands nta (nitrilotriacetate) and [15]aneN_4 (1,4,8,12-tetraazacyclopentadecane). They found no significant effect of acetate in the presence of nta, but a very significant effect for the [15]aneN_4 complex similar to that observed for the aquated system in the absence of a chelating ligand, from which it was concluded that acetate must occupy the trans coordination site of the Cr–C bond in order to induce the heterolysis reaction. Thus, the observed enhancement can be ascribed to a trans-labilization effect of coordinated acetate on the Cr–C bond.[5–7]

As the study of the heterolysis of Cr–C σ bonds is considered a model for the study of such reactions for transition metal–carbon σ bonds in general, it is of fundamental importance to resolve the detailed mechanism of the acetate-catalyzed reaction path. We have therefore performed a systematic kinetic study as a function of acetate concentration, temperature, and pressure for a series of complexes of the type LCr–R^{2+}, with L = H_2O, nta, and [15]aneN_4 and R = CH_2OH and $C(CH_3)_2OH$, in order to determine the associated activation parameters for the acetate-catalyzed reaction. The results of this study suggest a dissociatively activated heterolysis process involving an interchange ligand substitution reaction with a solvent molecule.

Experimental Section

Materials. Chromium(II) solutions were prepared by dissolving chromium metal powder (Aldrich) in 1 M $HClO_4$ (3 g of Cr in 150 mL 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 0.5 M Cr(II) solution. The ligands nta (EGA Chemie) and [15]aneN_4 (Aldrich) were used as purchased. 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).

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(2) Cohen, H.; Meyerstein, D. *Inorg. Chem.* **1974**, *13*, 2434.

(3) Espenson, J. H. *Adv. Inorg. Bioinorg. Mech.* **1982**, *1*, 1.

(4) Schmidt, W.; Swinehart, J. H.; Taube, H. *J. Am. Chem. Soc.* **1971**, *93*, 1117.

(5) Cohen, H.; Meyerstein, D. *Inorg. Chem.* **1984**, *23*, 84.

(6) (a) Rotman, A.; Cohen, H.; Meyerstein, D. *Inorg. Chem.* **1985**, *24*, 4158. (b) Masarwa, M.; Cohen, H.; Meyerstein, D.; Hickman, D. L.; Bakac, A.; Espenson, J. H. *J. Am. Chem. Soc.* **1988**, *110*, 4293.

(7) Ogino, H.; Shimura, M.; Tanaka, N. *J. Chem. Soc., Chem. Commun.* **1983**, 1063.

(8) Hart, E. J.; Thomas, J. K.; Gordon, S. *J. Phys. Chem.* **1964**, *68*, 1271, 1524.

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Measurements. The Cr(II) concentration was determined spectrophotometrically by following the reduction of $Co(NH_3)_5Cl^{2+}$ at 532 nm (ϵ = 49.6 M^{-1} cm^{-1}).[9] UV-vis spectra were recorded on Varian CARY 1 and Shimadzu UV-250 spectrophotometers. The pH of test solutions were measured using a Metrohm 632 instrument under argon atmosphere. Ambient-pressure kinetic measurements were performed on a Durrum D110 stopped-flow instrument, whereas experiments at elevated pressure were performed using a homemade high-pressure stopped-flow unit.[10] Both instruments were thermostated to ±0.1 °C. Data acquisition and handling were performed on on-line computer systems[11] using the OLIS KINFIT[12] set of programs.

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 (3) occurs.[6]

$$LCr(H_2O)_2^{2+} + H_2O_2 \rightarrow LCr(H_2O)_2^{3+} + OH^- + {}^{\bullet}OH$$

$$^{\bullet}OH + HCR_1R_2OH \rightarrow {}^{\bullet}CR_1R_2OH + H_2O$$

$$^{\bullet}CR_1R_2OH + LCr(H_2O)_2^{2+} \rightarrow L(H_2O)Cr\text{-}CR_1R_2OH^{2+} + H_2O \tag{3}$$

In the present experiments at least a 10% excess of L was employed and acetate was added to the Cr(II) solution prior to mixing. The rate constant for the reaction of $^{\bullet}OH$ with alcohols is $>8 \times 10^8$ M^{-1} s^{-1},[13] whereas the reaction of $^{\bullet}OH$ with acetate is considerably slower (8.5×10^7 M^{-1} s^{-1})[13] and does not interfere under the selected experimental conditions. Throughout this study $[Cr(II)] \geq 2 \times 10^{-3}$ and $[H_2O_2] \geq 4 \times 10^{-4}$ M, and since the rate constant for the first step in reaction 3 is $\geq 6 \times 10^4$ M^{-1} s^{-1}, the formation of the organochromium complex terminates in less than 40 ms. It follows that any heterolysis reaction with a half-life longer than ca. 50 ms can be studied using this procedure.

Results

Ambient-Pressure Studies. The heterolysis reactions of a series of (α-hydroxyalkyl)chromium(III) complexes $(H_2O)_5Cr\text{-}R^{2+}$, *trans*-([15]aneN_4)(H_2O)Cr-R^{2+}, and *cis*(nta)(H_2O)Cr-R^-, R = CH_2OH and $C(CH_3)_2OH$, were studied using the stopped-flow technique described above. Solutions containing H_2O_2 ((4–20) × 10^{-4} M) were mixed with solutions containing Cr(II) ((4–6) × 10^{-3} M), nta or [15]aneN_4 ((4.8–7.2) × 10^{-3} M), acetate (0–0.8 M), the organic solute (MeOH or *i*-PrOH, 1–2.4 M), and $NaClO_4$ to maintain the required ionic strength. The heterolysis reactions were studied at 321 and 400 nm and exhibited excellent first-order behavior for at least 3 half-lives of the reaction. The reaction is significantly accelerated by the presence of acetate, and the experimental results are reported in the form of k_{obs} versus $[CH_3COO^-]$ plots in Figure 1 for all investigated complexes.

The temperature dependence of the reactions was studied at different acetate concentrations, and the corresponding activation parameters (ΔH^* and ΔS^*) are summarized in Table I.

High-Pressure Studies. The pressure dependence of the heterolysis reactions, up to 150 MPa,[14] was studied for most complexes at different acetate concentrations. The observed rate constants decrease with increasing pressure, and plots of ln k_{obs} versus pressure are linear within the experimental error limits. The corresponding volumes of activation were calculated from the slopes of such plots ($-\Delta V^*/RT$) in the usual way[15] and are summarized in Table II.

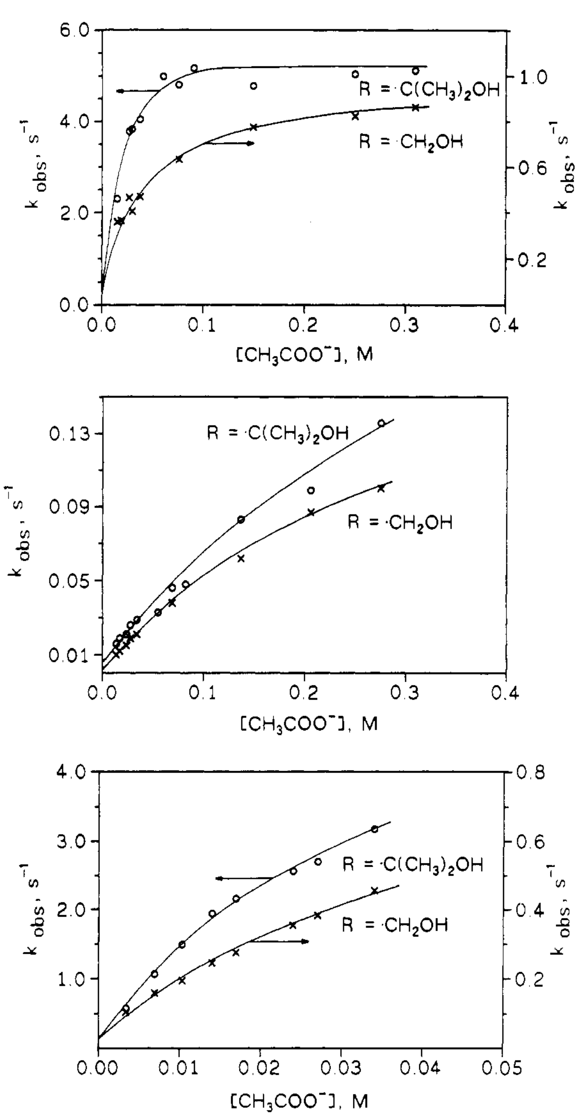

Figure 1. Plots of k_{obs} versus $[CH_3COO^-]$ for the heterolysis of (L)Cr-R^{2+}. Experimental conditions: $[Cr(II)] = 3.0 \times 10^{-3}$ M; $[H_2O_2] = 3.0 \times 10^{-4}$ M; [alcohol] = 0.5 M; ionic strength = 0.5 M. Key: (a, top) L = $(H_2O)_5$, pH = 5.3; (b, middle) L = (nta)(H_2O), pH = 5.1; (c, bottom) L = ([15]aneN_4)(H_2O), pH = 5.1.

Discussion

Aquated Cr(II) ions tend to undergo complex formation with acetate ions (Ac^-) in aqueous solution according to the reactions outlined in (4), for which K_1 = 15 M^{-1}, K_2 = 5 M^{-1}, and K_3 = 2.2×10^4 M^{-1}.[16] These equilibrium constants predict that mainly $Cr(H_2O)_6^{2+}$ and $Cr(H_2O)_5Ac^+$ are present at $[Ac^-] \leq 0.04$ M, whereas considerably higher concentrations of the dimeric species are produced at higher acetate concentrations. UV-vis spectra of Cr(II)–acetate mixtures were recorded for the different complexes as a function of acetate concentration up to 0.4 M at

$$Cr(H_2O)_6^{2+} + Ac^- \overset{K_1}{\rightleftharpoons} Cr(H_2O)_5Ac^+ + H_2O$$

$$Cr(H_2O)_5Ac^+ + Ac^- \overset{K_2}{\rightleftharpoons} Cr(H_2O)_4(Ac)_2 + H_2O$$

$$2Cr(H_2O)_4(Ac)_2 \overset{K_3}{\rightleftharpoons} [Cr(H_2O)(Ac)_2]_2 + 6H_2O \tag{4}$$

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(9) Guenther, P. R.; Linck, R. G. *J. Am. Chem. Soc.* **1969**, *91*, 3769.

(10) van Eldik, R.; Palmer, D. A.; Schmidt, R.; Kelm, H. *Inorg. Chim. Acta* **1981**, *50*, 131.

(11) Kraft, J.; Wieland, S.; Kraft, U.; van Eldik, R. *GIT Fachz. Lab.* **1987**, *31*, 560.

(12) OLIS Inc., Jefferson, GA 30549, Version 3.0 (1989).

(13) Buxton, G. V.; Greenstock, C. L.; Helman, W. P.; Ross, A. B. *J. Phys. Chem. Ref. Data* **1988**, *17*, 513.

(14) The previous high-pressure stopped-flow design reported in ref 10 was modified to enable kinetic measurements in a pressure range up to 200 MPa.

(15) van Eldik, R.; Asano, T.; le Noble, W. J. *Chem. Rev.* **1989**, *89*, 549.

(16) (a) Cannon, R. D.; Stillman, J. S. *Inorg. Chem.* **1975**, *14*, 2202. (b) Cannon, R. D.; Gholami, J. G. *J. Chem. Soc., Dalton Trans.* **1976**, 1574. (c) Cannon, R. D.; Gholami, J. G. *Bull. Chem. Soc. Jpn.* **1982**, *55*, 594.

Table I. Rate and Activation Parameters for the Heterolysis of (α-Hydroxyalkyl)chromium(III)[a]

complex	$[CH_3COO^-]$, M	k_{obs} at 25 °C, s^{-1}	$\Delta H^‡$, kJ mol^{-1}	$\Delta S^‡$, J K^{-1} mol^{-1}
$(H_2O)_5Cr{-}CH_2OH^{2+}$	0.015	0.27	65.1 ± 0.7	−37 ± 2
	0.31	0.82	70 ± 2	−11 ± 8
$(H_2O)_5Cr{-}C(CH_3)_2OH^{2+}$	0.015	3.4	67 ± 3	−9 ± 10
	0.31	5.4	61 ± 1	−25 ± 4
trans-([15]aneN_4)(H_2O)$Cr{-}CH_2OH^{2+}$ [b]	0.024	0.32	58.3 ± 0.8	−58 ± 3
trans-([15]aneN_4)(H_2O)$Cr{-}C(CH_3)_2OH^{2+}$ [b]	0.024	2.8	49.6 ± 0.3	−70 ± 1

[a] Experimental conditions: [Cr(II)] = 3.0×10^{-3} M, $[H_2O_2] = 3.0 \times 10^{-4}$ M, [alcohol] = 0.5 M, pH = 5.3, ionic strength = 0.5 M. [b] [[15]aneN_4] = 3.2 ± 10^{-3} M; pH = 5.1.

Table II. Volumes of Activation for the Heterolysis of (α-Hydroxalkyl)chromium(III) at 25 °C

L	$[CH_3COO^-]$, M	pH	[Cr(II)], M	$[H_2O_2]$, M	[*i*-PrOH], M	[MeOH], M	μ, M	$\Delta V^‡$, cm^3 mol^{-1}
H_2O	0.015	5.3	3×10^{-3}	3×10^{-4}	0.5		0.50	+15.1 ± 0.8
	0.31	5.3	3×10^{-3}	3×10^{-4}	0.5		0.50	+11.3 ± 0.6
	0.0032	5.0	2.5×10^{-3}	4×10^{-4}	1.0		0.013	+14.2 ± 0.5
	0.0085	5.5	2×10^{-3}	2×10^{-4}	1.1		0.016	+13.2 ± 0.9
	0.0069	5.1	2.5×10^{-3}	4×10^{-4}	1.0		0.017	+15.9 ± 0.3
	0.0063	5.0	2.5×10^{-3}	1×10^{-3}	1.0		0.017	+14.7 ± 0.3
	0.027	5.3	2.5×10^{-3}	4×10^{-4}	1.0		0.037	+12.5 ± 0.8
	0.16	4.8	2.5×10^{-3}	4×10^{-4}	1.0		0.31	+9.2 ± 0.2
	0.015	5.3	3×10^{-3}	3×10^{-4}		0.5	0.50	+10.7 ± 0.5
	0.31	5.3	3×10^{-3}	3×10^{-4}		0.5	0.41	+6.1 ± 0.4
	0.038	5.3	2.5×10^{-3}	4×10^{-4}		1.0	0.057	+11.2 ± 0.2
	0.076	5.3	2.5×10^{-3}	4×10^{-4}		1.0	0.11	+10.0 ± 0.6
	0.17	4.9	2.5×10^{-3}	4×10^{-4}		1.0	0.31	+8.9 ± 0.4
	0.26	6.6	2.5×10^{-3}	4×10^{-4}		1.0	0.31	+6.4 ± 0.3
nta[a]	0.017	5.1	3×10^{-3}	3×10^{-4}	0.5		0.50	+4.6 ± 0.3
	0.27	5.1	3×10^{-3}	3×10^{-4}	0.5		0.50	+4.8 ± 0.5
	0.024	5.1	3×10^{-3}	3×10^{-4}		0.5	0.50	+7.2 ± 0.7
	0.27	5.1	3×10^{-3}	3×10^{-4}		0.5	0.50	+7.4 ± 0.7
[15]aneN_4[b]	0.028	5.1	3×10^{-3}		0.5		0.51	+14.1 ± 1.4
	0.014	5.1	3×10^{-3}			0.5	0.50	+14.0 ± 0.7

[a] [nta] = 3.2×10^{-3} M. [b] [[15]aneN_4] = 3.2×10^{-3} M.

pH 5.1. In the case of $Cr(H_2O)_6^{2+}$ and *trans*-Cr([15]aneN_4)(H_2O)$_2^{2+}$ addition of 0.4 M acetate results in the formation of new absorption bands at 328 and 490 nm, which are due to the formation of the dimeric species. This means that the [15]aneN_4 complex is not stable in the presence of excess acetate and is converted to the dimeric species. For this reason the acetate concentration range was restricted to 0.035 M in the case of the [15]aneN_4 system, for which no evidence for the formation of dimeric species was observed. No significant spectral changes were observed on the addition of a high concentration of acetate to the nta complex, indicating that no dimeric species are formed in that case.

At low acetate concentrations the unsubstituted Cr(II) complexes react with the aliphatic free radicals $^\bullet R$ according to reaction 5, for which the second-order rate constant is (5–20) ×

$$LCr(H_2O)_2^{\,2+} + {}^\bullet R \rightarrow L(H_2O)Cr{-}R^{2+} + H_2O \tag{5}$$

10^7 M^{-1} s^{-1}.[2] The effect of acetate on the rate of the reaction of $Cr(H_2O)_6^{2+}$ with $^\bullet C(CH_3)_2OH$ was studied using the pulse-radiolysis technique. N_2O-saturated solutions containing 1×10^{-3} M Cr^{2+}, 0–0.27 M CH_3COONa, and 0.9 M $CH(CH_3)_2OH$ at pH 5.2 ± 0.2 (pH of the solution in the absence of acetate was 4.1) were irradiated. The following apparent rates of reaction were measured: 6.4×10^7, 7.3×10^7, 4.9×10^7, and 2.0×10^7 M^{-1} s^{-1} for $[CH_3COONa]$ = 0, 9×10^{-3}, 5×10^{-2}, and 0.27 M, respectively. These results demonstrate that the rate of reaction of the free radicals $^\bullet R$ with the various Cr(II) species produced in the presence of acetate decreases somewhat for the acetate complexes, but it remains to be a very fast step. Furthermore, the produced $L(H_2O)Cr{-}R^{2+}$ species can undergo substitution with acetate if it possesses labile water molecules to produce complexes of the type $L(Ac)Cr{-}R^+$. The latter processes are expected to be fast reactions and should occur prior to the studied heterolysis reactions.[3,7] In order to prove this, a series of experiments were performed in which acetate was not added to the Cr(II) solution prior to the formation of $L(H_2O)Cr{-}R^{2+}$ (see Experimental Section) but after the formation of $L(H_2O)Cr{-}R^{2+}$. Indeed the observed heterolysis rate constants were independent of the method employed and demonstrate that $L(H_2O)Cr{-}R^{2+}$ reacts very rapidly with acetate to produce the equilibrium mixture with $L(Ac)Cr{-}R^+$. Furthermore, a series of experiments were performed in which the Cr(II) concentration was gradually increased at a fixed acetate concentration. In this way the concentration of the dimeric species could be varied, but again the observed heterolysis rate constant remained constant for Cr(II) concentrations between 3×10^{-3} and 1.0×10^{-2} M.

The results in Figure 1 clearly demonstrate that the rate constant for heterolysis increases significantly with increasing acetate concentration in both the aquated Cr(II) and [15]aneN_4 systems. A limiting rate constant is reached at high acetate concentrations for the aquated Cr(II) system, which is up to 4 orders of magnitude larger than the spontaneous heterolysis rate constants in the absence of acetate. These observations are in excellent agreement with those reported before.[5–7] By way of comparison, the effect of acetate on the heterolysis of the nta complex is relatively small. The saturation of k_{obs} at high acetate concentrations (see Figure 1a) can be explained in terms of the participation of an acetato complex in the heterolysis reaction process.[5–7] A general reaction scheme is presented in (6), for

$$\begin{tikzcd}
L(H_2O)Cr{-}R^{2+} + Ac^- \arrow[r, shift left, "K_4"] \arrow[d, "+H_2O"', "k_1"] & L(Ac)Cr{-}R^+ + H_2O \arrow[l, shift left] \arrow[d, "+H_2O"', "k_2"] \\
L(H_2O)Cr{-}OH^{2+} + RH & L(Ac)Cr{-}OH^+ + RH
\end{tikzcd} \tag{6}$$

$$k_{obs} = \frac{k_1 + k_2K_4[Ac^-]}{1 + K_4[Ac^-]} \tag{7}$$

which the corresponding rate expression is given in (7). In this general scheme L represents $(H_2O)_4$, [15]aneN_4, or nta^{3-}. Furthermore, it involves a rapid pre-equilibration step with acetate,

Table III. Rate and Equilibrium Constants for the Spontaneous and Acetate-Catalyzed Heterolysis of Chromium–Carbon σ Bonds at 25 °C

complex	k_1,[a] s^{-1}	k_2,[b] s^{-1}	K_4,[b] M^{-1}	k_2K_4,[c] $M^{-1}\ s^{-1}$
$(H_2O)_5Cr{-}CH_2OH^{2+}$	6.6×10^{-4}	0.95 ± 0.02	26.0 ± 0.9	24.7 ± 1.1
$(H_2O)_5Cr{-}C(CH_3)_2OH^{2+}$	3.3×10^{-3}	6.1 ± 0.2	46 ± 10	282 ± 25
trans-$([15]aneN_4)(H_2O)Cr{-}CH_2OH^{2+}$	$<2 \times 10^{-2}$			11.3 ± 0.3
trans-$([15]aneN_4)(H_2O)Cr{-}C(CH_3)_2OH^{2+}$	2.0×10^{-3}	6.4 ± 0.1	29.6 ± 1.7	187 ± 17
cis$(nta)(H_2O)Cr{-}CH_2OH^-$	2.5×10^{-3}	0.15 ± 0.02	5.1 ± 0.8	0.76 ± 0.06
cis-$(nta)(H_2O)Cr{-}C(CH_3)_2OH^-$	3.8×10^{-3}	0.10 ± 0.02	12.3 ± 2.1	1.28 ± 0.08

[a] Determined in the absence of acetate (see also ref 6). [b] Determined from a plot of k_{obs}^{-1} versus $[CH_3COO^-]^{-1}$. [c] Slope of k_{obs} versus $[CH_3COO^-]$.

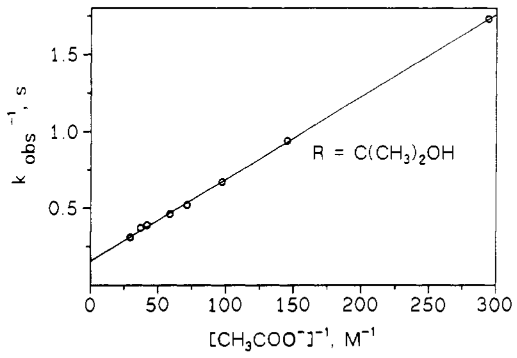

Figure 2. Typical plot of k_{obs}^{-1} versus $[CH_3COO^-]^{-1}$ for the heterolysis of *trans*-$([15]aneN_4)(H_2O)Cr{-}R^{2+}$. Experimental conditions: [Cr(II)] = 3.0×10^{-3} M; $[H_2O_2]$ = 3.0×10^{-4} M; $[([15]aneN_4)]$ = 3.2×10^{-3} M; ionic strength = 0.5 M; [alcohol] = 0.5 M.

as mentioned before[5-7] and demonstrated above. (7) predicts a linear dependence of k_{obs} on $[Ac^-]$ at low $[Ac^-]$ with an intercept k_1 (spontaneous heterolysis rate constant) and slope k_2K_4. k_1 could be measured directly in the absence of added acetate. At higher $[Ac^-]$ when K_4 is large, (7) predicts strong curvature in the plots of k_{obs} versus $[Ac^-]$ with a limiting rate constant $k_{obs} = k_2$ at high $[Ac^-]$, i.e. where $1 + K_4[Ac^-] \approx K_4[Ac^-]$. For the curves in Figure 1a,c, (7) can be simplified to (8) since the

$$k_{obs} = k_2K_4[Ac^-]/\{1 + K_4[Ac^-]\} \qquad (8)$$

uncatalyzed path is much slower (see k_1 values in Table III), and a double-reciprocal plot procedure can be adopted to evaluate k_2 and K_4. A correction for the contribution of k_1 has no significant influence. A typical example is shown in Figure 2, and the results are summarized in Table III.

The results in Table III clearly demonstrate the very impressive catalytic effect of acetate ions on the heterolysis process. The rate enhancement especially observed for the aquated Cr(III) and $[15]aneN_4$ systems is ascribed to a trans-labilization effect of coordinated acetate. On the basis of our experimental observations reported above and the general trend that metal–carbon σ bond labilize the trans coordination position, it is reasonable to expect that acetate will mainly occupy the trans position in the presence of an excess of Ac^-. Once acetate is coordinated, it obviously influences the metal–carbon bond strength and causes a trans labilization, similar to that found for coordinated hydroxy ligands; viz., solvent exchange on $Cr(H_2O)_5OH^{2+}$ is 2 orders of magnitude faster than on $Cr(H_2O)_6^{3+}$.[17] This is a rather novel finding since acetate is in general a weak nucleophile. The values of K_4 are relatively large and in good agreement with those published before.[5-7] The absence of a significant catalytic effect for the nta system is also in agreement with the above arguments, since no trans solvent molecules can be substituted by acetate in this system. The significantly smaller K_4 value is probably due to the negative charge on $(nta)(H_2O)Cr{-}R^-$. Definitely, the structure of the $(nta)(H_2O)Cr{-}R^-$ complex must involve the N donor atom trans to the organic aliphatic residue since no significant catalytic effect of the acetate moieties (nta ligand) on the heterolysis reaction was observed in the absence of added acetate.[6a] A similar explanation probably accounts for the absence of such an effect on the spontaneous heterolysis of $(edta)Cr{-}R^{2-}$, as R was also suggested to occupy a position trans to one of the N donor atoms.[18] The values of k_2 and K_4 also differ quite considerably for R = CH_2OH and $C(CH_3)_2OH$ for a particular system. In the case of the aquated and $[15]aneN_4$ systems, k_2 and K_4 are significantly larger for R = $C(CH_3)_2OH$ than for R = CH_2OH. Thus, trans labilization effects of the coordinated R seem to control the value of K_4, whereas trans labilization by coordinated acetate has a larger accelerating effect for the R = $C(CH_3)_2OH$ complex.

The activation parameters reported in Tables I and II were measured at different acetate concentrations and therefore represent, depending on the exact $[Ac^-]$ dependence of k_{obs} (see Figure 1), the data for either k_2K_4 or k_2 at low or high acetate concentrations, respectively. The $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ data in Table I exhibit no specific trend between the high and low acetate concentrations. The values of $\Delta S^{\ddagger}$ for k_2 (i.e. at high acetate concentration) are all significantly negative indicating that bond formation with a solvent molecule must be of significance during heterolysis of the metal–carbon σ bond.

The $\Delta V^{\ddagger}$ data in Table II exhibit some very interesting and consistent trends. Throughout the series of measurements for the aquated Cr(II) system, an increase in the acetate concentration causes a decrease in $\Delta V^{\ddagger}$ to less positive values. Typically $\Delta V^{\ddagger}$ has a value of ca. +14 $cm^3\ mol^{-1}$ at low acetate concentration, i.e. where $k_{obs} = k_2K_4[Ac^-]$, compared to values around +8 $cm^3\ mol^{-1}$ at high acetate concentration, i.e. where $k_{obs} = k_2$. This trend is independent of the organic radical R, pH, or ionic strength of the medium. Since $\Delta V^{\ddagger}(k_2K_4) = \Delta V^{\ddagger}(k_2) + \Delta V(K_4)$, where the latter term represents the reaction volume for the formation of $L(Ac)Cr{-}R^+$ in (6), it follows that the difference of ca. 6 $cm^3\ mol^{-1}$ between the $\Delta V^{\ddagger}$ values measured at low and high acetate concentrations, respectively, must be due to the contribution of $\Delta V(K_4)$. In terms of the general mechanism, K_4 involves substitution of a coordinated water molecule by acetate, which is accompanied by charge neutralization and an overall volume increase. The $\Delta V^{\ddagger}(k_2)$ values of between +7 and +9 $cm^3\ mol^{-1}$ clearly demonstrate that the catalyzed heterolysis process (k_2) is dissociatively activated and resembles values usually found for a dissociative interchange (I_d) type of substitution mechanism.[15,19] In the case of the nta complex, the observed $\Delta V^{\ddagger}$ is independent of the acetate concentration and represents the combined effect for k_2K_4 (i.e. slope of k_{obs} versus $[Ac^-]$). For this system the catalytic effect (k_2K_4) is much smaller than observed for the other investigated systems (see Table III), which is mainly related to a significantly smaller k_2 value. The small positive $\Delta V^{\ddagger}$ values can be interpreted in terms of a $\Delta V^{\ddagger}(k_2)$ value of ca. +8 $cm^3\ mol^{-1}$ and a $\Delta V(K_4)$ value of −1 to −4 $cm^3\ mol^{-1}$. The latter is quite reasonable for the substitution of a water molecule on *cis*-$(nta)(H_2O)Cr{-}R^-$ by acetate since this will lead to charge concentration accompanied by a volume collapse.

All the measured volumes of activation support a dissociatively activated heterolysis reaction for the acetate-induced process and can be related to the trans-labilization effect of coordinated acetate

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(17) Akitt, J. W.; Merbach, A. E. In *NMR Basic Principles and Progress*; Springer: New York, 1990; Vol. 24, p 189.

(18) Ogino, H.; Shimura, M.; Tanaka, N. *Inorg. Chem.* **1982**, *21*, 126.

(19) Van Eldik, R.; Merbach, A. E. *Comments Inorg. Chem.* **1992**, *12*, 341.

in the two systems that exhibit remarkable acceleration in the presence of acetate. By way of comparison, ΔV^{*} for the spontaneous heterolysis of the chromium–carbon bond was found to be almost zero[20] 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. Thus, bond breaking and bond making seem to cancel in terms of volume changes and nicely fit the general concept of an interchange substitution mechanism on the Cr(III) center. The significantly more positive ΔV^{*} values found in this study for the acetate-catalyzed heterolysis reaction favor the operation of a dissociative interchange mechanism (I_d) during which the chromium–carbon bond breakage is accompanied by bond formation with the entering solvent molecule. The more dissociatively activated interchange process compared to the spontaneous heterolysis reaction must be related to the trans-labilization effect of the coordinated acetate ions. Furthermore, ΔV^{*} at high acetate concentration (i.e. for k_2) is larger for R = $C(CH_3)_2OH$ than for R = CH_2OH in the aquated system. This observation is in good agreement with the suggested I_d mechanism in which Cr–R bond breakage will cause a volume increase that will depend on the size of R. This is not observed for the [15]aneN_4 system, which is probably related to the bulkiness of this ligand such that the size of R will not play such a crucial role in determining the value of ΔV^{*}. In terms of an interchange mechanism, it follows that both the uncatalyzed and catalyzed heterolysis reactions involve the attack of a solvent molecule on the chromium–carbon bond, in agreement with earlier suggestions.[5,6a]

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Registry No. $(H_2O)_5Cr-CH_2OH^{2+}$, 32108-95-5; $(H_2O)_5Cr-C(CH_3)_2OH^{2+}$, 32108-93-3; *trans*-([15]aneN_4)$(H_2O)Cr-CH_2OH^{2+}$, 98737-23-6; *trans*-([15]aneN_4)$(H_2O)Cr-C(CH_3)_2OH^{2+}$, 98737-24-7; *cis*-(nta)$(H_2O)Cr-CH_2OH^-$, 96163-65-4; *cis*-(nta)$(H_2O)Cr-C(CH_3)_2OH^-$, 98760-07-7.

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(20) Sisley, M. J.; Rindermann, W.; van Eldik, R.; Swaddle, T. W. *J. Am. Chem. Soc.* **1984**, *106*, 7432.