Influence of Acetate Ion on the Formation Reactions of Organochromium(III) Species. A Rapid-scan and High-pressure Pulse-radiolysis Study

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A UV/VIS rapid-scan technique was employed to study the formation of organochromium(III) species that are characterized by absorbance maxima at 321 and 412 nm. The effect of acetate on this formation reaction was studied, and spectral measurements demonstrated that it is mainly the monomeric chromium(II) acetate species that react with the alkyl radical, no involvement of the dimeric species being found. A high-pressure pulse-radiolysis technique was employed to study the effect of pressure on the formation of such complexes. The observed volumes of activation exhibit a decrease from +5.7 to −7.4 cm^3 mol^{-1} on increasing the acetate concentration from 0 to 0.27 mol dm^{-3}. Similar measurements in the presence of phosphate did not indicate any significant effect on the observed volume of activation for the formation of the metal–carbon bond. This difference can be interpreted in terms of the pressure dependence of the dimerization of chromium(II) acetate complexes, which was measured independently and exhibits a reaction volume of +38 ± 4 cm^3 mol^{-1}. It is concluded that the mechanism of the formation of chromium–carbon σ bonds is not affected by anions such as acetate and phosphate.

It has been known for quite some time that aliphatic free radicals react readily with aquated chromium(II) species to produce organochromium(III) species having relatively stable chromium–carbon σ bonds.[1,2] The aliphatic free radicals can be produced *via* the reaction of the aliphatic molecules (RH) with ˙OH radicals, which can either be produced *via* pulse radiolysis of N_2O-saturated solutions or *via* the modified Fenton reaction as indicated in equation (1).[2-4] In general the organochromium(III) species subsequently undergo heterolysis reactions as indicated in equation (2).[2] Therefore, the latter are in many cases only short-lived intermediates, and rapid-scan techniques are required to obtain spectral information on them.

$$\left.\begin{array}{l}[Cr(H_2O)_6]^{2+} + H_2O_2 \longrightarrow \\ \quad [Cr(H_2O)_5(OH)]^{2+} + {}^{\bullet}OH + H_2O \\ \quad RH + {}^{\bullet}OH \longrightarrow {}^{\bullet}R + H_2O \\ [Cr(H_2O)_6]^{2+} + {}^{\bullet}R \longrightarrow [Cr(H_2O)_5R]^{2+} + H_2O\end{array}\right\} \quad (1)$$

$$[Cr(H_2O)_5R]^{2+} + H_2O \longrightarrow [Cr(H_2O)_5(OH)]^{2+} + RH \quad (2)$$

We recently performed a detailed study of the effect of pressure on the reaction of various aliphatic free radicals ˙R with $[Cr(H_2O)_6]^{2+}$ to produce $[Cr(H_2O)_5R]^{2+}$ by using a high-pressure pulse-radiolysis technique.[5] All reactions exhibited a small positive volume of activation (average value for 10 different radicals +4.3 ± 1.0 cm^3 mol^{-1}), which was interpreted as evidence that chromium–carbon σ-bond formation is controlled by solvent exchange on $[Cr(H_2O)_6]^{2+}$ and follows an I_d mechanism.

It has been shown in a number of studies that acetate and related anions can catalyse the heterolysis reaction (2) *via* trans-labilization of the metal–carbon σ bond.[3,6-9] It is known that acetate co-ordinates very rapidly to an aquated chromium(II) to produce various complexes as shown in equations (3)–(5).[10-12]

$$[Cr(H_2O)_6]^{2+} + O_2CMe^- \overset{K_1}{\rightleftharpoons} [Cr(H_2O)_5(O_2CMe)]^+ + H_2O \quad (3)$$

$$[Cr(H_2O)_5(O_2CMe)]^+ + O_2CMe^- \overset{K_2}{\rightleftharpoons} [Cr(H_2O)_4(O_2CMe)_2] + H_2O \quad (4)$$

$$2[Cr(H_2O)_4(O_2CMe)_2] \overset{K_3}{\rightleftharpoons} [\{Cr(H_2O)(O_2CMe)_2\}_2] + 6H_2O \quad (5)$$

The equilibrium constants K_1 to K_3 are known, such that a detailed speciation is possible. However, it is not known what effect acetate and related anions have on the formation reactions of organochromium(III) species due to their influence on the speciation and reactivity of the chromium(II) species. It is of fundamental importance to elucidate the possible catalytic effect of such anions in chromium(II/III) chemistry.

We have therefore employed rapid-scan and high-pressure pulse-radiolysis techniques to gain more information on the effect of anions such as acetate, and by way of comparison phosphate, on the formation of short-lived alkylchromium(III) species.

Experimental

All chemicals were of analytical reagent grade (Merck) and used without further purification. The preparation of the test solutions was recently described in detail.[8] The rapid-scan

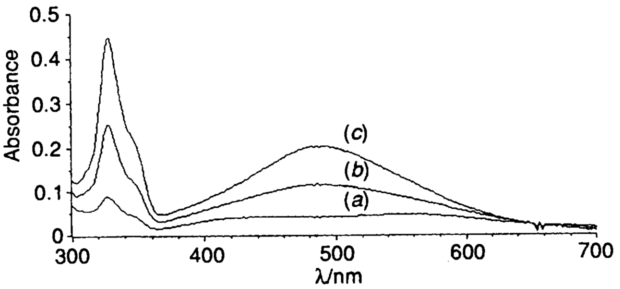

Fig. 1 Spectra of chromium(II) with various concentrations of added acetate: $[Cr^{II}]_T = 3.0 \times 10^{-3}$, $[acetate]_T = 0.018$ (*a*), 0.046 (*b*), 0.32 (*c*) mol dm^{-3}; pH 5.3

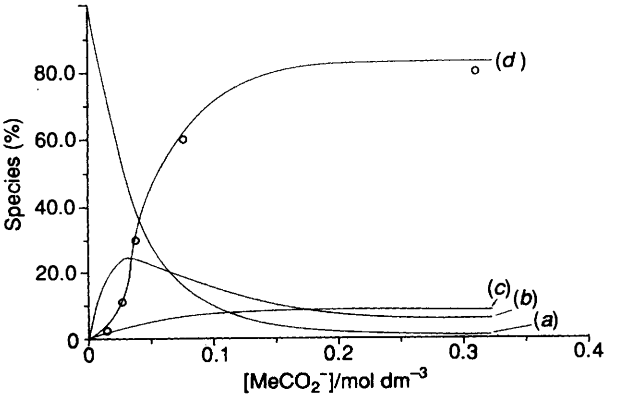

Fig. 2 Calculated concentration of chromium(II) acetate species with increasing acetate concentration: (*a*) $[Cr(H_2O)_6]^{2+}$, (*b*) $[Cr(H_2O)_5(O_2CMe)]^+$, (*c*) $[Cr(H_2O)_4(O_2CMe)_2]$ and (*d*) $[Cr_2(H_2O)_2(O_2CMe)_4]$; $[Cr^{II}]_T = 3 \times 10^{-3}$ mol dm^{-3}. Curves are predicted according to the reactions (3)–(5); points are experimental results from spectral measurements

spectra were recorded with an optical simultaneous multichannel analyser (OSMA; Spectroscopy Instruments, Gilching, Germany) coupled to a Durrum D110 stopped-flow instrument. This analyser has a reference and signal channel, which are matched before a measurement to ensure a low background absorbance. This adjustment was made with solvent in the observation chamber of the stopped-flow and the recorded spectrum was used as background for the subsequent measurements. The UV/VIS spectra of chromium(II) solutions recorded on a Cary 1 spectrophotometer were used to calibrate the wavelength scale of the OSMA detector. Similarly, these spectra were used to calibrate the absorbance scale of the rapid-scan measurements. The scan time of the instrument was 33 ms per spectrum with a maximum number of 10 spectra per kinetic run. Further details on the OSMA system as used in this study are reported elsewhere.[13]

Details of the high-pressure equipment used in the pulse radiolysis work are given elsewhere.[14,15] Other experimental details are similar to those adopted for the ambient-pressure studies or related high-pressure studies.[3,6–8] The pulse-radiolysis experiments were carried out using a Varian 7715 linear accelerator at the Hebrew University of Jerusalem with a 200 mA current of 5 MeV (*ca.* 8×10^{-13} J) electrons and 0.1–1.5 μs pulses of electrons. Details on the optical detection system are given elsewhere.[16]

Results and Discussion

Formation of Organochromium(III) *in the Presence of Acetate.*—In the presence of acetate $[Cr(H_2O)_6]^{2+}$ rapidly forms a series of acetato complexes as summarized in equations (3)–(5).[10–12] These species exhibit characteristic UV/VIS spectra, the dimeric species having a prominent peak at 490 nm (ε = 143 dm^3 mol^{-1} cm^{-1}). The equilibrium distribution of the different chromium(II) acetate complexes is controlled by the acetate and chromium(II) concentrations. The spectra reported in Fig. 1 clearly show how an increase in acetate concentration results in an increase in the dimer concentration (as observed by an absorbance increase at 490 nm). In addition, the spectra exhibit a peak at 328 nm and a shoulder at 345 nm, which are also ascribed to the presence of the dimer. Under these conditions the speciation as a function of acetate concentration, based on the values $K_1 = 15$, $K_2 = 5$ and $K_3 = 2.2 \times 10^4$ dm^3 mol^{-1},[10–12] can be presented as in Fig. 2. The experimental observations are within the experimental error limits in good agreement with the speciation predicted by the reactions (3)–(5). At higher acetate concentrations the dimer concentration reaches a limiting value, as indicated by Fig. 2, and it becomes the main species in solution.

The formation and heterolysis of $[Cr(H_2O)_5R]^{2+}$ recorded in the presence of acetate was studied for R = $C(CH_3)_2OH$. Repetitive scan spectra recorded for different acetate concentrations under such conditions (see Fig. 3) indicate a significant increase in absorbance between 320 and 330 nm due to the formation of CrR^{2+} species *via* the modified Fenton reaction (1). This is followed by an absorbance decrease due to the subsequent heterolysis reaction (2). The overall difference between the spectrum before and after the reaction in Fig. 3(*b*) is negligible, indicating that the dimer concentration remained constant. Typical absorbance *vs.* time plots at 328 and 490 nm are reported in Fig. 4. At 0.31 mol dm^{-3} acetate 80% of the total chromium(II) concentration is present in the dimeric form. In these experiments 3×10^{-4} mol dm^{-3} H_2O_2 was used, which

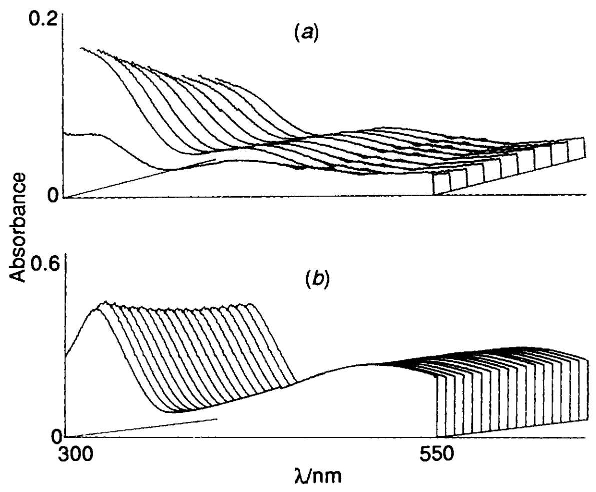

Fig. 3 Formation and heterolysis of the Cr–C σ bond detected by three-dimensional rapid scan measurements. $[Cr^{II}]_T = 3 \times 10^{-3}$, $[Pr^iOH] = 0.5$, $[H_2O_2] = 3 \times 10^{-4}$ mol dm^{-3}; Δt = 33 ms; pH 5.3; I = 0.5 mol dm^{-3}. $[MeCO_2^-]$ = 0.015 (*a*), 0.31 mol dm^{-3} (*b*)

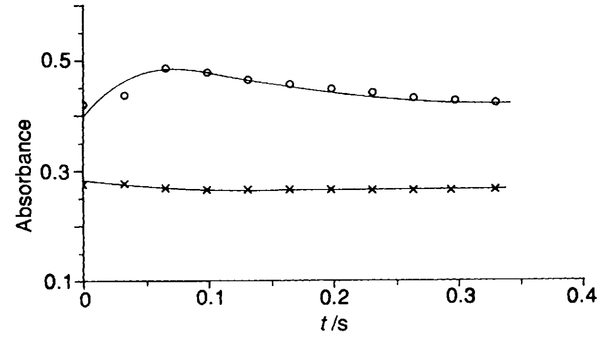

Fig. 4 Absorbance *versus* time at 328 (○) and 490 nm (×) [from Fig. 3(*b*)]. The point at $t = 0$ is the starting spectrum, that at $t = 0.033$ s is the first rapid-scan spectrum, and subsequent points correspond to successive intervals of 33 ms on the rapid-scan time-scale

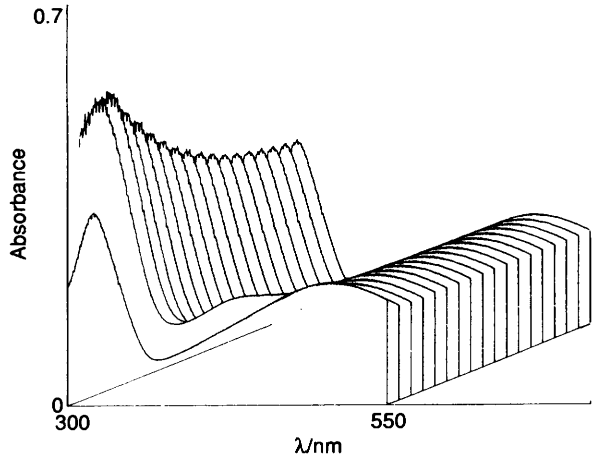

Fig. 5 Formation and heterolysis of the Cr–C σ bond detected by rapid-scan measurements: $[Cr^{II}]_T = 3 \times 10^{-3}$, $[MeCO_2^-] = 0.31$, $[Pr^iOH] = 0.5$, $[H_2O_2] = 6 \times 10^{-4}$ mol dm^{-3}; $\Delta t = 33$ ms; pH 5.3; $I = 0.5$ mol dm^{-3}

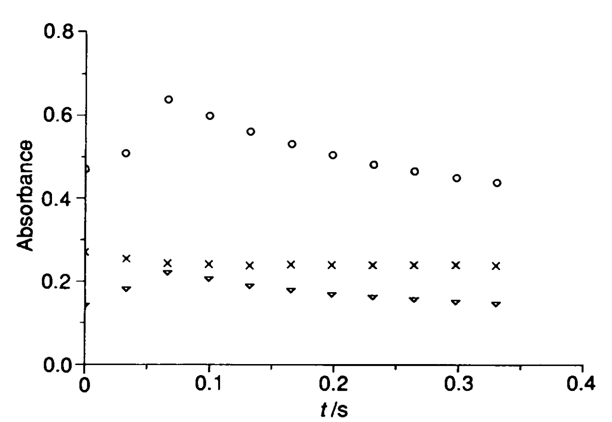

Fig. 6 Absorbance *versus* time at 328 (○), 412 (▽) and 490 nm (×) (from Fig. 5). The point at $t = 0$ is the starting spectrum, that at $t = 0.033$ s is the first rapid-scan spectrum, and subsequent points correspond to successive intervals of 33 ms on the rapid-scan time-scale

Table 1 Rate constants as a function of pressure for the formation of $[Cr(H_2O)_5\{C(CH_3)_2OH\}]^{2+}$ in the absence and presence of acetate[a]

	$10^{-4}k_{obs}$[b]/s^{-1}		
$MeCO_2^-$/mol dm^{-3}	$P = 0.1$	150 MPa	$\Delta V^‡$/cm^3 mol^{-1}
0	6.4	4.5	+5.7
0.009	7.3	5.0	+6.0
0.050	4.9	6.2	−3.9
0.27	1.9	3.0	−7.4

[a] Experimental conditions: N_2O-saturated solution; 1×10^{-3} mol dm^{-3} total Cr^{II}; 0.9 mol dm^{-3} Pr^iOH; pH 5.2 ± 0.2 (pH 4.1 in the absence of acetate); 20 °C; $\lambda = 390$ nm. [b] Mean from at least six kinetic runs.

means that 6×10^{-4} mol dm^{-3} Cr^{II} is consumed during the formation of CrR^{2+} [see equation (1)]. This predicts a 20% decrease in the chromium(II) concentration, which would result in a significantly larger absorbance decrease when the dimeric species are involved. The observed spectral changes suggest that it is mainly the monomeric species that react with H_2O_2, followed by a rapid equilibration[10] without any significant decrease in the dimer concentration. On increasing the H_2O_2 concentration the observed effects should be more significant since a higher concentration of the alkylchromium(III) species is produced. This is demonstrated in Fig. 5, where the H_2O_2 concentration was increased to 6×10^{-4} mol dm^{-3}. The absorbance changes (increase and subsequent decrease) are much larger than at the lower H_2O_2 concentration, and the new peak at 412 nm can be assigned to the organochromium(III) species.[17,18] Under these conditions 1.2×10^{-3} mol dm^{-3} Cr^{II} should be used, which represents 40% of the total chromium(II) concentration when the reaction goes to completion. Again no evidence for direct participation of the dimeric species could be found. Absorbance *vs.* time plots at 328, 412 and 490 nm (Fig. 6) demonstrate that the maximum absorbance at 328 and 412 nm is found 0.1 s after mixing, which indicates that Cr–R bond formation must be complete during this time.

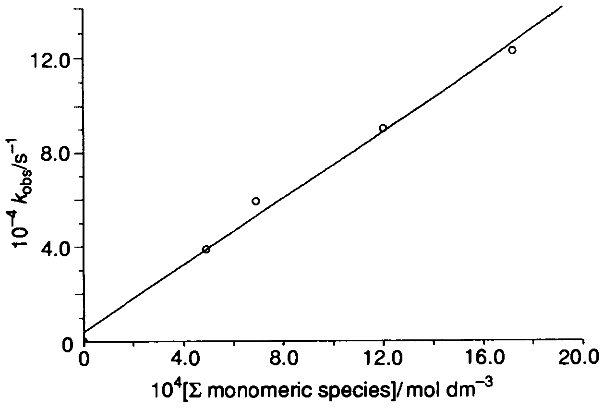

Fig. 7 Plot of k_{obs} *versus* calculated [monomeric species] for the formation of the complex with a Cr–C σ bond. Experimental conditions: $[Pr^iOH] = 0.5$, $[MeCO_2^-] = 0.08$ mol dm^{-3}; pH 5.2; $I = 0.5$ mol dm^{-3}; N_2O-saturated solutions

These observations are in excellent agreement with indirect kinetic evidence[7,8] in favour of the monomeric species being the main reaction partners, even under conditions where 80% of Cr^{II} is present in the dimeric form. Cannon and co-workers[10,17,19] demonstrated that dissociation of the dimer occurs prior to electron transfer with $[Cr(NH_3)_5X]^{2+}$ (X = halide), polydentate ligands, or I_3^- complexes.

The effect of pressure on the observed rate of formation of $[Cr(H_2O)_5\{C(CH_3)_2OH\}]^{2+}$ was studied in the absence and presence of O_2CMe^-. The main results at low and high pressure are reported in Table 1, along with the corresponding volumes of activation. The atmospheric data clearly show that k_{obs} decreases almost by a factor of three on increasing the acetate concentration to 0.27 mol dm^{-3}. Furthermore, the small positive volume of activation typical for the formation of CrR^{2+} species[5] in the absence of acetate becomes significantly negative at high acetate concentrations. These observations must be related to the formation of chromium(II) acetate species, especially the dimers.

The decrease in k_{obs} with increasing $[MeCO_2^-]$ at ambient conditions (see Table 1) correlates well with the fact that *ca.* 80% of the Cr^{II} will be present in the dimeric form [see equations (3)–(5)] at high acetate concentration. This means a reduction in the concentration of the monomeric species by a factor of 4, which agrees well with the decrease in k_{obs} observed under such conditions. The observed rate constant increases with increasing $[Cr^{II}]_T$ in a non-linear way, in agreement with earlier observations,[10] due to the interference of the equilibria (3)–(5). This dependence becomes approximately linear when expressed in terms of the sum of the [monomeric species] (see Fig. 7). This observation indicates that the dimeric species do not react with the organic free radicals to form chromium–carbon σ bonds, whereas the different monomeric species seem to react in a similar way as demonstrated by the very similar rate data observed in the absence and presence of low acetate concentrations.

In order to describe this observation in a more quantitative way, the equilibria (3)–(5) are summarized by an overall equilibrium (6) between the di- and mono-meric species, where

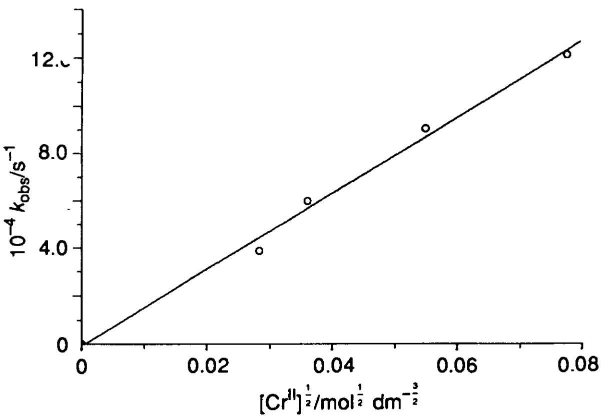

Fig. 8 Plot of k_{obs} *versus* $[Cr^{II}]_T^{\frac{1}{2}}$ for the formation of the complex with a Cr–C σ bond. Experimental conditions as in Fig. 7

$$[\{Cr(H_2O)(O_2CMe)_2\}_2] \underset{}{\overset{K_4}{\rightleftharpoons}} 2\,Cr_{mono} \qquad (6)$$

$$Cr_{mono} + {}^{\bullet}R \xrightarrow{k} Cr\text{–}R^{2+} \qquad (7)$$

Cr_{mono} represents all the monomer species, *i.e.* $[Cr(H_2O)_6]^{2+}$, $[Cr(H_2O)_5(O_2CMe)]^+$ and $[Cr(H_2O)_4(O_2CMe)_2]$. The overall equilibrium K_4 (which corresponds to K_D in ref. 11) can be expressed by equation (8),[11] and its value depends on the

$$K_4^{\frac{1}{2}} = K_3^{-\frac{1}{2}}\{(K_1K_2[MeCO_2^-]^2)^{-1} + (K_2[MeCO_2^-])^{-1} + 1\} \qquad (8)$$

acetate concentration selected. The value of $[Cr_{mono}]$ can be estimated from the total chromium(II) concentration, $[Cr]_T$, and K_4 as shown in equations (9) and (10). At high $[MeCO_2^-]$, equation (8) predicts a decrease in K_4 such that equation (10) can be simplified to (11). In terms of the mechanism given in equations (6) and (7), the observed rate constant for the formation of the CrR^{2+} species can be expressed as in equation (12). It follows that k_{obs} should vary linearly with $[Cr_{mono}]$ (see Fig. 7) and with $[Cr]_T^{\frac{1}{2}}$ (see Fig. 8). The latter correlation is quite acceptable when the above-outlined simplifications are taken into account.

$$\begin{aligned}[Cr]_T &= [Cr_{mono}] + 2[dimer] \\ &= [Cr_{mono}] + (2[Cr_{mono}]^2/K_4) \qquad (9)\end{aligned}$$

$$[Cr_{mono}] = \tfrac{1}{4}\{-K_4 + (K_4^2 + 8[Cr]_TK_4)^{\frac{1}{2}}\} \qquad (10)$$

$$[Cr_{mono}] \approx ([Cr]_TK_4/2)^{\frac{1}{2}} \qquad (11)$$

$$k_{obs} = k[Cr_{mono}] = k(K_4[Cr]_T/2)^{\frac{1}{2}} \qquad (12)$$

The significant decrease in $\Delta V^{\ddagger}$ for the formation of complexes with a Cr–C bond with increasing acetate concentration is presumably also related to the effect of pressure on the formation of the dimeric species in equations (3)–(5). In order to investigate this aspect further the UV/VIS spectra of different chromium(II) solutions containing 0.32 mol dm^{-3} acetate at pH 5.3 were recorded as a function of pressure (a typical example is given in Fig. 9). The $[\{Cr(H_2O)(O_2CMe)_2\}_2]$ species which absorbs at 328 and 490 nm decreases significantly in concentration at elevated pressure, *i.e.* pressure assists the formation of monomeric species. These spectral measurements were used to determine the dimer concentration and K_4 as a function of pressure in two different ways. First (Table 2), the absorption coefficient (ε) of 143 dm^3 mol^{-1} cm^{-1} at 490 nm[11] was used to estimate [dimer], from which $[Cr_{mono}]$ and K_4 could be estimated at a fixed $[MeCO_2^-]$ and at various $[Cr]_T$. Secondly (Table 3), the method adopted by Cannon and Gholami[11] was used in which a non-linear fit of absorbance at 490 nm (A) as a function of $[Cr]_T$ at each pressure was performed using equation (13) (where l is the optical pathlength) and the cited value of ε. The two treatments result in significantly negative values for $\Delta\bar{V}(K_4)$, indicating that dissociation of the dimer is accompanied by a volume collapse, presumably due to the co-ordination of additional solvent molecules and an increase in electrostriction resulting from the dissociation of acetate anions. Thus pressure will favour the dissociation of the dimer, cause an increase in the concentration of the monomeric species, and so increase the rate of the chromium–carbon bond-formation process.

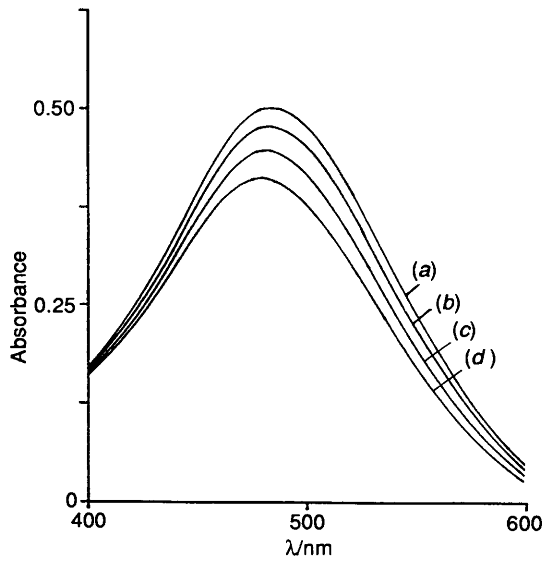

Fig. 9 Pressure dependence of the absorption spectrum of the dimer in the chromium(II) acetate equilibrium. Experimental conditions: $[Cr^{II}] = 7.4 \times 10^{-3}$, $[MeCO_2^-] = 0.32$ mol dm^{-3}. Pressure = 5 (*a*), 50 (*b*), 100 (*c*) and 150 MPa (*d*)

$$[Cr]_T = (2A/\varepsilon l) + (K_4A/\varepsilon l)^{\frac{1}{2}} \qquad (13)$$

According to the rate equation (12), k_{obs} will be proportional to $kK_4^{\frac{1}{2}}$, such that $\Delta V^{\ddagger}(k_{obs}) = \Delta V^{\ddagger}(k) + \frac{1}{2}\Delta\bar{V}(K_4)$. In the absence of added acetate, $\Delta V^{\ddagger}$ will represent the reaction of $[Cr(H_2O)_6]^{2+}$ with ${}^{\bullet}R$, and the value of +5.7 cm^3 mol^{-1} is in good agreement with data reported for such reactions.[5] A similar value was found at low $[MeCO_2^-]$, which indicates that all monomeric species react with ${}^{\bullet}R$ in a similar way, *i.e.* Cr–R bond formation is controlled by dissociation of a co-ordinated solvent molecule in terms of an I_d mechanism.[5] It is therefore safe to conclude that $\Delta V^{\ddagger}(k) = +6$ cm^3 mol^{-1}. At high $[MeCO_2^-]$, $\Delta V^{\ddagger}(k_{obs}) = \Delta V^{\ddagger}(k) + \frac{1}{2}\Delta\bar{V}(K_4) = +6 + \frac{1}{2}(-38) = -13$ cm^3 mol^{-1}, which is in agreement with the trend of negative $\Delta V^{\ddagger}$ values observed under such conditions (Table 1). Thus the observed pressure dependence of the dimer–monomer equilibrium constant, K_4, can account for the observed trend in the $\Delta V^{\ddagger}$ data in Table 1.

We have also investigated the temperature dependence of the dimer–monomer equilibrium by recording UV/VIS spectra as a function of temperature at different $[Cr]_T$ (see Fig. 10 for a typical example). The data were treated in the same way as for the pressure-dependence study and are summarized in Table 4. The small positive ΔS° values presumably arise from the overall dissociation of the dimer into monomeric species. Our ΔH° values are in agreement with that reported,[20] *viz. ca.* 20 kJ mol^{-1}.

Formation of Organochromium(III) *in the Presence of Phos-*

Table 2 Equilibrium constant K_4 as a function of pressure calculated using a mass-balance procedure*

$10^3[Cr^{II}]_T$/mol dm^{-3}	P/MPa	Absorbance at 490 nm	10^3[Dimer]/mol dm^{-3}	10^4K_4/mol dm^{-3}	$\Delta\bar{V}(K_4)$/cm^3 mol^{-1}
7.4	5	0.4805	3.36	1.38	−36 ± 2
	50	0.4565	3.19	3.26	
	100	0.4292	3.00	6.53	
	150	0.4000	2.80	11.57	
6.0	5	0.3904	2.73	1.07	−36 ± 3
	50	0.3755	2.63	2.08	
	100	0.3556	2.49	4.18	
	150	0.3263	2.28	9.09	
4.5	5	0.3020	2.11	0.37	−44 ± 5
	50	0.2860	2.00	1.25	
	100	0.2655	1.86	3.27	
	150	0.2556	1.79	4.73	
3.0	5	0.1844	1.29	1.37	−36 ± 3
	50	0.1724	1.21	2.78	
	100	0.1541	1.08	6.53	
	150	0.1395	0.98	10.82	
			mean:		−38 ± 4

* $[MeCO_2^-]$ = 0.32 mol dm^{-3}, pH 5.3, 25 °C, ionic strength = 0.5 mol dm^{-3}, optical pathlength = 1 cm.

Table 3 Equilibrium constant K_4 as a function of pressure calculated with a non-linear fit of equation (13)

P/MPa	10^4K_4*/mol dm^{-3}
5	0.83
50	2.08
100	5.26
150	9.71
$\Delta\bar{V}$/cm^3 mol^{-1}	−38 ± 3

* Experimental data taken from Table 2.

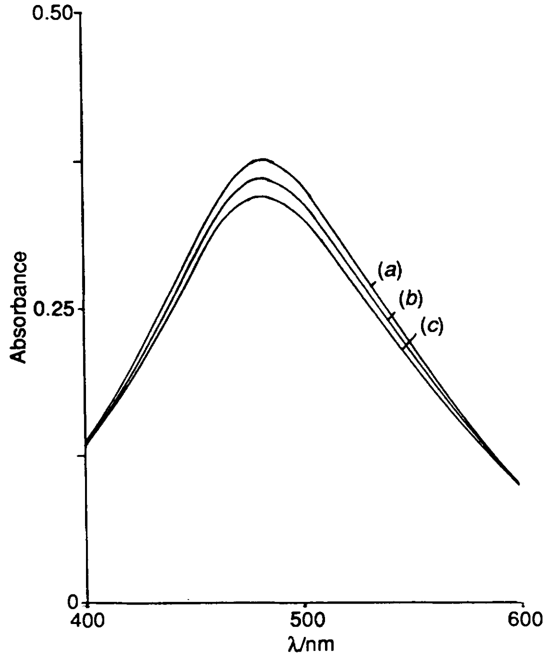

Fig. 10 Temperature dependence of the absorption spectrum of the dimer in the chromium(II)–acetate equilibrium. Experimental conditions: $[Cr^{II}]_T = 6 \times 10^{-3}$, $[MeCO_2^-]$ = 0.32 mol dm^{-3}. Temperature = 15 (*a*), 25 (*b*) and 35 °C (*c*)

phate.—By way of comparison, a series of experiments were performed in which phosphate was used instead of acetate, since phosphate is known to also catalyse the heterolysis reaction of CrR^{2+}. On addition of $H_2PO_4^-$ to Cr^{II} at pH 3.2 a 1:1 chromium(II)–phosphate complex is produced, although there is no significant spectral change that accompanies this reaction.[9] A typical set of repetitive scan spectra recorded during the formation and decomposition of CrR^{2+} in the presence of $H_2PO_4^-$ is given in Fig. 11. A new absorbance peak is produced between 300 and 320 nm, but the overall absorbance changes are much smaller than in the presence of acetate. No evidence for the formation of a dimeric chromium(II) species exists in the case of phosphate. The main reactive species under the conditions selected is $[Cr(H_2O)_5(HPO_4)]$ (deprotonation of co-ordinated $H_2PO_4^-$ due to a lowering of the pK_a value on co-ordination), which binds ˙R to produce $[Cr(H_2O)_4(HPO_4)R]$.

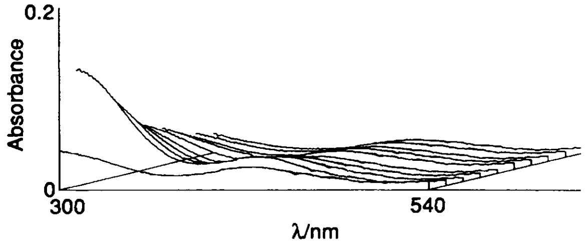

Fig. 11 Formation and heterolysis of the Cr–C σ bond in the presence of $H_2PO_4^-$ as detected by rapid-scan measurements: $[Cr^{II}]_T = 3 \times 10^{-3}$, $[H_2PO_4^-]$ = 0.37, $[Pr^iOH]$ = 0.5, $[H_2O_2] = 3 \times 10^{-4}$ mol dm^{-3}; Δt = 33 ms; pH 3.2; I = 0.5 mol dm^{-3}

In the case of the high-pressure pulse-radiolysis studies, addition of 0.27 mol dm^{-3} $H_2PO_4^-$ to the chromium(II) solution instead of acetate resulted in an ambient k_{obs} value of 1.0×10^5 s^{-1} and a $\Delta V^\ddagger$ of +4.2 cm^3 mol^{-1}. These values are very similar to those obtained in the absence of the anion (see Table 1), indicating that the formation of CrR^{2+} is not significantly affected by the presence of $H_2PO_4^-$, presumably since there is no formation of dimeric species as in the case of acetate.

Conclusion

The spectral data reported in this study nicely supplement all the indirect kinetic evidence and clearly demonstrate that in the presence of anions such as acetate and phosphate it is the monomeric complexes with Cr^{II} that react with ˙R to produce the CrR^{2+} species. The presence of an anionic ligand in the co-ordination sphere of Cr^{II} could labilize the *trans* water molecule which can then be replaced by ˙R to form the metal–carbon σ bond. However, this must not be the case since aquated Cr^{II} is

Table 4 Equilibrium constant K_4 as a function of temperature[a]

$10^3[\mathrm{Cr}]_T$/mol dm^{-3}	T/°C	Absorbance at 490 nm	10^3[Dimer]/mol dm^{-3}	$10^4 K_4$[b]/mol dm^{-3}	ΔH°/kJ mol	ΔS°/J K^{-1} mol^{-1}
6.0	15.0	0.3793	2.65	1.85	44 ± 3	84 ± 10
	25.0	0.3608	2.52	3.66		
	35.0	0.3435	2.39	6.23		
4.5	15.0	0.2651	1.85	3.46	35 ± 3	57 ± 8
	25.0	0.2500	1.75	5.71		
	35.0	0.2347	1.64	9.07		
2.25	15.0	0.1292	0.90	2.25	36 ± 3	57 ± 8
	25.0	0.1229	0.86	3.27		
	35.0	0.1114	0.78	6.10		
	15.0			2.34[c]	36 ± 4	58 ± 10
	25.0			4.19[c]		
	35.0			6.32[c]		

[a] $[\mathrm{MeCO_2}^-]$ = 0.32 mol dm^{-3}; pH 5.3; ionic strength = 0.5 mol dm^{-3}; P = 0.1 MPa; optical pathlength = 1 cm. [b] Calculated using a mass-balance procedure unless otherwise indicated, see text. [c] Calculated using a non-linear fit of equation (13) and a fixed ε value, see text.

extremely labile and inclusion of anionic ligands in the co-ordination sphere does not necessarily increase its lability.

The results of this investigation clearly demonstrate that the major route for the formation of chromium–carbon bonds is *via* the reaction with the non-dimeric species, *i.e.* the aquated chromium(II) ions. The process is controlled by solvent exchange on $\mathrm{Cr^{II}}$,[5] which is very rapid in the case of the hexaaqua and other monomeric species. Thus, the rate constant for bond formation decreases with increasing acetate concentration due to the corresponding decrease in concentration of the monomeric species. Under pressure, the dimer dissociates and causes an increase in the concentration of the monomers, accompanied by an increase in the observed rate constant. Thus the observed decrease in $\Delta V^\ddagger$ on increasing acetate concentration is not due to a changeover in mechanism in the presence of acetate, but rather due to a shift in the equilibrium concentration of the reactive chromium(II) species. Such effects were not observed for the addition of phosphate since no evidence for the formation of dimeric or phosphate-substituted species of $\mathrm{Cr^{II}}$ exists. In terms of the earlier studied acetate-catalysed heterolysis reactions of $\mathrm{CrR^{2+}}$ species,[8] it is obvious that acetate can rapidly co-ordinate to $\mathrm{CrR^{2+}}$, *via trans*-labilization of the metal–carbon σ bond, to induce the heterolysis reaction. Again these effects are accompanied by significant changes in $\Delta V^\ddagger$, which can be accounted for in terms of a dissociatively activated heterolysis process.[8]

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References

1 H. Cohen and D. Meyerstein, *Inorg. Chem.*, 1974, **13**, 2434.
2 J. H. Espenson, *Adv. Inorg. Bioinorg. Mechan.*, 1982, **1**, 1; A. Bakac and J. H. Espenson, *Inorg. Chem.*, 1983, **22**, 779 and refs. therein.
3 A. Rotman, H. Cohen and D. Meyerstein, *Inorg. Chem.*, 1985, **24**, 4158.
4 M. Masarwa, H. Cohen, D. Meyerstein, D. L. Hickman, A. Bakac and J. H. Espenson, *J. Am. Chem. Soc.*, 1988, **110**, 4293.
5 R. van Eldik, W. Gaede, H. Cohen and D. Meyerstein, *Inorg. Chem.*, 1992, **31**, 3695.
6 H. Cohen and D. Meyerstein, *Inorg. Chem.*, 1984, **23**, 84.
7 H. Ogino, M. Shimura and N. Tanaka, *J. Chem. Soc., Chem. Commun.*, 1983, 1063.
8 H. Cohen, W. Gaede, A. Gerhard, D. Meyerstein and R. van Eldik, *Inorg. Chem.*, 1992, **31**, 3805.
9 W. Gaede, R. van Eldik, H. Cohen and D. Meyerstein, *Inorg. Chem.*, in the press.
10 R. D. Cannon and J. S. Stillman, *Inorg. Chem.*, 1975, **14**, 2202.
11 R. D. Cannon and J. G. Gholami, *J. Chem. Soc., Dalton Trans.*, 1976, 1574.
12 R. D. Cannon and J. G. Gholami, *Bull. Chem. Soc. Jpn.*, 1982, **55**, 594.
13 A. Gerhard, W. Gaede, A. Neubrand, V. Zang, R. van Eldik and P. Stanitzeck, *Rev. Sci. Instrum.*, submitted for publication.
14 M. Spitzer, F. Gärtig and R. van Eldik, *Rev. Sci. Instrum.*, 1988, **59**, 2092.
15 S. F. Whishart and R. van Eldik, *Rev. Sci. Instrum.*, 1992, **63**, 3224.
16 S. Goldstein, G. Czapski, R. van Eldik, H. Cohen and D. Meyerstein, *J. Phys. Chem.*, 1991, **95**, 1281.
17 R. D. Cannon and J. S. Stillman, *Inorg. Chem.*, 1975, **14**, 2207.
18 G. W. Kirker, A. Bakac and J. H. Espenson, *J. Am. Chem. Soc.*, 1982, **104**, 1249.
19 L. M. Wilson and R. D. Cannon, *Inorg. Chem.*, 1985, **24**, 4366.
20 R. D. Cannon, *J. Chem. Soc. A*, 1968, 1098.

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