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Volumes of activation for β-elimination and related reactions of chromium(III)–alkyl complexes in aqueous solutions

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Abstract

A systematic study of the effect of pressure on the decomposition of chromium(III)–alkyl complexes via β-elimination was undertaken. It was found that the elimination of OR (R=H or alkyl) is characterized by a negative volume of activation, whereas the elimination of NH_3 exhibits a positive volume of activation. These values are interpreted in terms of early and late transition states, respectively. In addition, the effect of pressure on the spontaneous and acid-catalyzed heterolysis of $[(H_2O)_5Cr^{III}–CH_2CH(OH)_2]^{2+}$ and $[(H_2O)_5Cr^{III}–H]^{2+}$ was studied. The results, when compared to literature data, indicate that the volumes of activation for heterolysis depend strongly on the intimate nature of the mechanism.

Keywords: Volume of activation; β-Elimination; Chromium complexes; Alkyl complexes

1. Introduction

Over the last three decades the interest in chemical reactions involving complexes with metal–carbon bonds has increased appreciably. This is mainly due to the fact that such species are key intermediates in many chemical processes, viz. degradation of important biological systems [1], and formation of C–C bonds via processes such as Fischer–Tropsch, hydro-formylation and metathesis catalyzed by metal ions [2].

Unstable complexes with metal–carbon σ bonds have been studied extensively in aqueous solution. It has for instance been reported that every aliphatic free radical reacts with chromous ions in aqueous solution via reaction (1) [3].

$$Cr^{2+}_{aq} + {}^{\bullet}CR^1R^2R^3 \longrightarrow [(H_2O)_5Cr^{III}–CR^1R^2R^3]^{2+} \quad (1)$$

The formal oxidation state of the chromium in the product is +3 and the organic ligand is formally a carbanion, but experimental evidence clearly indicates that the bond has a strong covalent character [3–5]. The stability of such complexes varies from half-lives of a few microseconds to several months [3,4]. The chromium(III)–carbon σ bond is cleaved in aqueous solution via homolysis or heterolysis as shown in reactions (2) and (3), respectively

$$[(H_2O)_5Cr^{III}–CR^1R^2R^3]^{2+} \rightleftharpoons Cr^{2+}_{aq} + {}^{\bullet}CR^2R^2R^3 \quad (2)$$

$$[(H_2O)_5Cr^{III}–CR^1R^2R^3]^{2+} \xrightarrow{H^+} Cr^{3+}_{aq} + HCR^1R^2R^3 \quad (3)$$

If the organic residue contains a good leaving group X on the carbon atom in the β position to the metal center, then the complex decomposes via β-elimination, as shown in Eq. (4), to produce the corresponding olefin and X^- as the final stable products. This reaction has so far been observed for halides, hydroxyls, ethers, phosphates and amines [1,3,6]. Reaction (4)

$$[(H_2O)_5Cr^{III}–CR^1R^2CR^3R^4X]^{2+} \longrightarrow Cr^{3+}_{aq} + R^1R^2C{=}CR^3R^4 + X^- \quad (4)$$

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also occurs for other metal–carbon σ bonds, viz. Cu(II), Co(III) and Fe(III) [7–9] and in other solvents [3]. The rate of this reaction for X = OH and OR is pH dependent.

More recently, we have shown that the application of high-pressure kinetic techniques can greatly assist the elucidation of the detailed mechanism of organometallic reactions [10]. This has also been shown to be the case for metal–carbon bonded complexes undergoing typical homolysis or heterolysis reactions [11]. We have therefore undertaken a systematic study of the effect of pressure on various β-elimination and related reactions of Cr(III)–carbon σ bonded complexes [3j,12]. The results are compared with those reported for typical heterolysis reactions.

2. Experimental

2.1. Materials

Analytical grade dioxane was used in this study and distilled, prior to use, after addition of some $FeSO_4$ and taking only the fraction between 100 and 102 °C. Research grade *cis*-2-butene, ethylene and propylene were supplied in lecture bottles (Phillips 66, Matheson and Messers. Griesheim). All chemicals were of analytical grade. Solutions were prepared with distilled water that was further purified by passing through a Q Millipore setup so that the final resistance was >10 MΩ/cm. Chromium(II) perchlorate (0.5 mol dm^{-3}) solutions were prepared by dissolving super pure chromium powder (BDH) in 1.0 mol dm^{-3} $HClO_4$, continuously purged with Ar, which was cleaned from traces of O_2 by passing it through a 0.5 mol dm^{-3} $Cr^{2+}{}_{aq}$ solution in a washbottle. Dilute $Cr^{2+}{}_{aq}$ solutions were prepared using syringe techniques [13]. All solutions were deaerated by bubbling Ar, He or N_2O through them for 15 min prior to use.

2.2. Irradiations

Pulse-radiolysis experiments were carried out with a Varian 7715 linear electron accelerator with a 200 mA current, 5 MeV electrons, using a transportable high pressure system with a modified four-window cell [14]. A 150 W Xenon arc lamp (Hamamatsu) (the high light intensity improved the signal to noise level of the kinetic traces), a grating double monochromator model DH-10 (Instruments SA, Inc.) and a R212 photomultiplier (Hamamatsu) were employed in the optical detection system. The photomultiplier signal was transferred through a Sony/Tektronix 390 AD programmable digitizer to a Micro PDP-11/24 computer, with which all kinetic traces were evaluated.

2.3. Stopped - flow measurements

Kinetic experiments at ambient pressure were performed on a Durrum D110 instrument. A home-made high-pressure stopped-flow unit [15] was employed for kinetic measurements at pressures up to 150 MPa. Both instruments were thermostated to within ±0.1 °C and connected to an on-line data acquisition system using OLIS KINFIT programs [16].

2.4. Production of aliphatic free radicals

Two alternative procedures were employed for the production of the aliphatic free radicals. In the pulse-radiolysis experiments irradiation of a neutral or slightly acidic, N_2O saturated solution ($pH>2.5$, $[N_2O]=2.2\times10^{-2}$ mol dm^{-3}), resulted in the following reactions [17].

$$H_2O \xrightarrow{\gamma,\, e^-} e^-{}_{aq},\ {}^{\bullet}H,\ {}^{\bullet}OH,\ H_2,\ H_2O_2,\ H_3O^+ \qquad (5)$$

$$e^-{}_{aq} + N_2O \xrightarrow{H^+} {}^{\bullet}OH + N_2$$
$$k=9.1\times10^9\ dm^3\ mol^{-1}\ s^{-1} \qquad (6)$$

The hydrated electron is transformed into hydroxyl radicals via reaction (6) in less than 1 μs. In solutions containing saturated aliphatic solutes, the ${}^{\bullet}OH$ radicals and hydrogen atoms rapidly produce aliphatic free radicals via the hydrogen abstraction reaction (7) [17].

$${}^{\bullet}OH/H^{\bullet} + HCR^1R^2R^3 \longrightarrow H_2O/H_2 + {}^{\bullet}CR^1R^2R^3$$
$$k_{OH}\geq 10^8\ dm^3\ mol^{-1}\ s^{-1} \qquad (7)$$
$$k_H\geq 10^5\ dm^3\ mol^{-1}\ s^{-1}$$

Thus in solutions containing >0.2 mol dm^{-3} t-butanol, >0.3 mol dm^{-3} diethyl ether[1] and >0.2 mol dm^{-3} ethanol, more than 90% of the primary radicals are transformed into the aliphatic free radical in less than 1 μs. In solutions containing 0.3 mol dm^{-3} Me_2SO, methyl radicals are formed via the following reaction sequence [19].

$${}^{\bullet}OH + (CH_3)_2SO \longrightarrow (CH_3)_2\dot{S}O(OH)$$
$$k=7\times10^9\ dm^3\ mol^{-1}\ s^{-1} \qquad (8)$$

$$(CH_3)_2\dot{S}O(OH) \longrightarrow {}^{\bullet}CH_3 + CH_3SOOH$$
$$k=1.5\times10^7\ s^{-1} \qquad (9)$$

In solutions containing 1×10^{-2} mol dm^{-3} ethylene or propylene, β-hydroxy free radicals are formed via the fast addition reactions (10) and (11) [17].

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[1] In the case of diethyl ether and ethanol some derived radicals, ${}^{\bullet}CH_2CH_2OCH_2CH_3$ and ${}^{\bullet}CH_2CH_2OH$, respectively, are also formed, but they account for only ≈13% of the overall yield [17,18].

$$^{\bullet}OH + H_2C{=}CH_2 \longrightarrow {}^{\bullet}CH_2CH_2OH$$

$$k = 6\times10^9\ dm^3\ mol^{-1}\ s^{-1} \qquad (10)$$

$$^{\bullet}OH + H_2C{=}CHCH_3 \longrightarrow {}^{\bullet}CH(CH_3)CH_2OH$$

$$k = 6\times10^9\ dm^3\ mol^{-1}\ s^{-1} \qquad (11)$$

In the stopped-flow experiments, the modified Fenton reaction was used to generate the aliphatic free radicals [3e] via reaction (12), followed by reactions (7), (8), (10) or (11) [1e].

$$Cr^{2+}{}_{aq} + H_2O_2 \longrightarrow CrOH^{2+}{}_{aq} + {}^{\bullet}OH$$

$$k = 7\times10^4\ dm^3\ mol^{-1}\ s^{-1} \qquad (12)$$

Thus in solutions containing 2×10^{-3} mol dm^{-3} $Cr^{2+}{}_{aq}$ all of the H_2O_2 will produce $^{\bullet}OH$ free radicals in less than 60 ms. The $^{\bullet}OH$ radicals react rapidly with the organic solutes via reactions (7) to (11) to produce the aliphatic radicals, which in turn rapidly bind to Cr^{2+} via reaction (1).

In both the radiolytic and stopped-flow experiments a possible competing reaction (13) may occur [17].

$$^{\bullet}OH + Cr^{2+}{}_{aq} \longrightarrow CrOH^{2+}{}_{aq}$$

$$k = 3\times10^9\ dm^3\ mol^{-1}\ s^{-1} \qquad (13)$$

Thus in all cases the experimental conditions were selected such that $k_{OH+RH}\,[RH] \gg k_{OH+Cr}\,[Cr^{2+}{}_{aq}]$.

The transient complexes $(H_2O)_5Cr^{III}$–R^{2+}, where R = CH_2CH_2OH, $CH(CH_3)CH_2OH$, $CH_2C(CH_3)_2OH$, $CHOCH_2CH_2OCH_2$, $CH_2C(CH_3)_2NH_3{}^+$ and H, were prepared via reaction (1). The spectral features and kinetics of formation and decomposition of these transient complexes at ambient pressure were previously reported [3f,i,j,12,20] and are therefore not discussed in detail herein. All the rates observed in this study are in accord with those reported in the literature [3f,i,j,12,20].

3. Results and discussion

3.1. β-Elimination reactions

The reaction of the various aliphatic free radicals produced in reactions (7) to (12) with $Cr^{2+}{}_{aq}$ in reaction (1) is characterized by the formation of a band around 390 to 405 nm depending on the nature of the radical. This band can be used to study the kinetics of formation and subsequent decomposition outlined in reactions (1) to (4) [11]. The reaction of $Cr^{2+}{}_{aq}$ with β-hydroxy radicals obtained via the addition of $^{\bullet}OH$ to ethylene or propylene, reactions (10) and (11), was studied using the stopped-flow and pulse-radiolysis techniques. These reactions lead to the formation of $[(H_2O)_5Cr^{III}$–$CH_2CH_2OH]^{2+}$ and $[(H_2O)_5Cr^{III}$–$CH(CH_3)CH_2OH]^{2+}$, respectively [3g,j], which subsequently undergo β-elimination in spontaneous and acid-catalyzed pathways [3g,j]. A systematic study of the effect of pressure on the β-elimination of $[(H_2O)_5Cr^{III}$–$CH_2CH_2OH]^{2+}$ at different pHs resulted in the $\Delta V^{\neq}$ data summarized in Table 1. The results indicate no specific pH dependence, demonstrating that both the spontaneous and acid-catalyzed pathways must involve very similar volume changes. The β-elimination of $[(H_2O)_5Cr^{III}$–$CH(CH_3)CH_2OH]^{2+}$ measured in this study exhibited a $\Delta V^{\neq}$ value of -5.8 ± 0.5 cm^3 mol^{-1} at pH 2.2, which is in close agreement with that reported in Table 1. Similar studies were performed with t-BuOH and 1,4-dioxane which produce the complexes $[(H_2O)_5Cr^{III}$–$CH_2C(CH_3)_2OH]^{2+}$ and $[(H_2O)_5Cr^{III}$–$CHOCH_2CH_2OCH_2]^{2+}$ respectively [3f,i]. The subsequent β-elimination reactions were studied at pH 4.2 and in 0.8 mol dm^{-3} $HClO_4$ and resulted in $\Delta V^{\neq}$ values of -6.3 ± 0.7 and -7.0 ± 0.8 cm^3 mol^{-1}, respectively. Once again these results demonstrate the pH independence of the $\Delta V^{\neq}$ value.

We conclude from these data that the nature of the transition state must be rather similar for both the spontaneous and acid-catalyzed reactions, which basically follow the same mechanism. Before we can propose a detailed mechanism, earlier conclusions have to be taken into account:

1. The first product in all β-elimination processes seems to be a π-complex between the leaving olefin and the central transition metal cation. It was pointed out that the latter complex is probably better described as somewhere between a π-complex and a cyclometallated form [3i,j].

2. It was shown that the rate-determining step involves the breaking of the C–X bond. This conclusion is based on the observation that the rate constants for the β-elimination processes are correlated with the C–X bond strength [12].

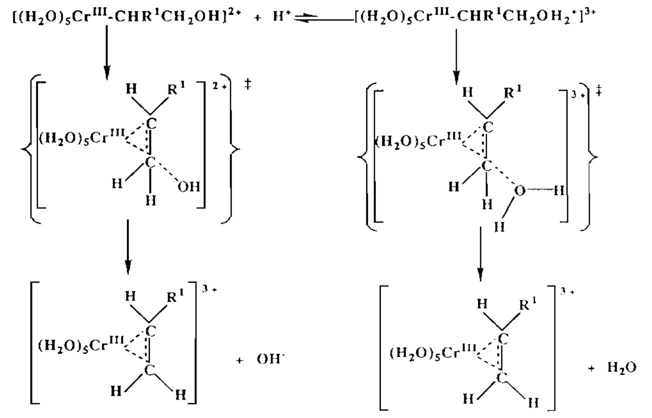
Thus, based on the present and previous results, it is proposed that the mechanism of β-hydroxyl elimination is best described by Scheme 1. The protonation equilibrium is not expected to involve a large overall volume change since it does not involve charge creation

Table 1

Summary of $\Delta V^{\neq}$ data found for the β-elimination of $(H_2O)_5Cr^{III}$–$CH_2CH_2OH^{2+}$ as a function of pH at 20 °C

$[Cr^{2+}]$ (mol dm^{-3})	$[H_2O_2]$ (mol dm^{-3})	pH	k_{obs}^{a} (s^{-1})	$\Delta V^{\neq}$ (cm^3 mol^{-1})
4×10^{-3}	2×10^{-4}	2.58	39±4	−4.1±0.2
1.2×10^{-3}	2×10^{-4}	3.05	18±2	−5.4±0.3
1×10^{-2}	2×10^{-3}	3.53	6.6±0.5	−3.6±0.3
5×10^{-3}	1.5×10^{-4}	3.67	7.5±0.8	−3.1±1.0
2×10^{-3}	1.5×10^{-4}	4.27	4.2±0.4	−5.4±0.4

^{a}Measured at 5 MPa.



Scheme 1.

or neutralization. For both pathways it is suggested that the transition state formation involves a coherent partial ring-closure process, which will be associated with a volume collapse and a stretching of the C–OH bond. The latter will be associated with a volume increase that will partially offset the volume collapse. Clearly in all the OR (R = H, alkyl) elimination reactions studied, the ring-closure process is the dominant factor in determining the sign of $\Delta V^{\neq}$.

We also studied the β-elimination of NH_3 from $[(H_2O)_5Cr^{III}\text{-}CH_2C(CH_3)_2(NH_3^+)]^{3+}$ [12]. The free radical $^{\cdot}CH_2C(CH_3)_2NH_3^+$ was produced via reaction (14). Its reaction with $Cr^{2+}{}_{aq}$ yields the desired

$$^{\cdot}OH + (CH_3)_3CNH_3^+ \longrightarrow H_2O + {}^{\cdot}CH_2C(CH_3)_2NH_3^+ \quad (14)$$

transient which decomposes via β-elimination to yield ammonia, 2-methyl-propene and $Cr^{3+}{}_{aq}$ [12a]. The rate of this reaction is independent of pH. The measured volume of activation for the β-elimination of NH_3 from this transient complex is $+3.1 \pm 1.0$ cm^3 mol^{-1}. $\Delta V^{\neq}$ for the analogous β-elimination from $[(H_2O)_nCu^{II}\text{-}CH_2C(CH_3)_2(NH_3^+)]^{2+}$ is $+3.6 \pm 1.0$ cm^3 mol^{-1}. Since only one copper system was studied, the similarity of the values for the chromium and copper systems might be incidental. It follows that the volume of activation for β-elimination of NH_3 from $[(H_2O)_5Cr^{III}\text{-}CH_2C(CH_3)_2(NH_3^+)]^{3+}$ is significantly larger (by ~10 cm^3 mol^{-1}) than that for the analogous β-elimination of OH^- from $[(H_2O)_5Cr^{III}\text{-}CH_2C(CH_3)_2OH]^{2+}$. A plausible source for this large difference is that the elimination of ammonia is considerably slower than the elimination of hydroxyl due to the fact that the C–N bond is stronger than the C–O bond in these compounds [12]. Thus a 'late', product-like, transition state, i.e. considerable dissociation of the C–N bond, is expected for the ammonia elimination, whereas an 'early', ring-closed, transition state is expected for the hydroxyl elimination as outlined above. On the basis of this argument, the observed pressure effects reveal fundamental information on the nature of the transition state in terms of 'early' and 'late', i.e. 'reactant' and 'product' like, respectively.

3.2. Heterolysis reactions

β-Elimination and heterolysis reactions of Cr(III) alkyl complexes exhibit the common feature of producing Cr(III) product species. It is therefore of interest to compare the volume changes associated with these processes.

Data reported for heterolysis reactions of Cr(III) alkyl complexes indicate an almost zero $\Delta V^{\neq}$ value for spontaneous and acid-catalyzed heterolysis [11a] compared to significantly positive $\Delta V^{\neq}$ values for anion-catalyzed heterolysis reactions [11d,f]. These data were interpreted in terms of interchange and dissociative interchange mechanisms, respectively. By way of comparison, we decided to measure, using the pulse-radiolysis technique, the pressure dependence of significantly faster, spontaneous and acid-catalyzed heterolysis reactions. Two such systems were studied.

1. The heterolysis of $[(H_2O)_5Cr^{III}\text{–}CH_2CH(OH)_2]^{2+}$ is a relatively fast reaction presumably due to the presence of the two hydroxyl groups [3f]. The observed volume of activation for the acid independent path, pH 4.2 and $k = 2.0$ s^{-1} at ambient pressure, is $+3.3$ cm^3 mol^{-1}, and for the acid dependent path, 0.2 mol dm^{-3} $[H_3O^+]$ and $k = 68$ s^{-1} at ambient pressure, is $+1.9$ cm^3 mol^{-1}. These results clearly indicate that although the reaction rates are relatively high, there is no major change in mechanism when compared to the earlier studied spontaneous and acid-catalyzed reactions [11a], i.e. the mechanism is in principle an interchange process characterized by relatively low volumes of activation.

In principle, the transient complex $[(H_2O)_5Cr^{III}\text{-}CH_2CH(OH)_2]^{2+}$ could also decompose via the β-elimination reaction

$$[(H_2O)_5Cr^{III}\text{-}CH_2CH(OH)_2]^{2+} \longrightarrow Cr(H_2O)_6{}^{3+} + CH_2{=}CHOH + OH^- \quad (15)$$

followed by $CH_2{=}CHOH \rightarrow CH_3CHO$ (we thank one of the reviewers for pointing out this possibility). However, the positive $\Delta V^{\neq}$ observed for the decomposition of $[(H_2O)_5Cr^{III}\text{–}CH_2CH(OH)_2]^{2+}$ seems to support the idea that the detailed mechanism involves the heterolysis of the chromium–carbon bond, rather than the β-elimination process.

2. The volume of activation for reaction (16) was measured using the pulse-radiolysis technique. Here the leaving group is indeed very small. For this fast,

$$[(H_2O)_5Cr^{III}\text{-}H]^{2+} + H_3O^+ \longrightarrow Cr^{3+}{}_{aq} + H_2 \quad (16)$$

acid-catalyzed reaction, $k = 1 \times 10^4$ dm^3 mol^{-1} s^{-1} [20], $\Delta V^{\neq} = -8.7$ cm^3 mol^{-1}, i.e. considerably more negative than reported for the other heterolysis reactions. This is probably related to the very small leaving group, significant charge concentration, and the partial binding of a solvent molecule, which together result in a negative volume of activation.

The data reported in this and earlier studies indicate the importance of various structural and electronic effects in tuning the intimate nature of the transition state of β-elimination and heterolysis reactions. Such effects result in quite different volumes of activation and associated transition states for formally the same process. The position of the transition state along the reaction coordinate can vary significantly depending on the nature of the reactant and so control the observed effects. This information is crucial in efforts to improve our mechanistic understanding of such processes.

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