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FULL PAPER

β-Hydride shift involvement in the acid catalysed decomposition of $[(H_2O)_5Cr^{III}–C(CH_3)_2OH]^{2+}$

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Received 13th July 1999, Accepted 6th September 1999

Propene has been found to be a major product of the acid catalysed decomposition of $[(H_2O)_5Cr^{III}–C(CH_3)_2OH]^{2+}$. It is proposed that this complex isomerizes *via* a β-hydride shift step to form $[(H_2O)_5Cr^{III}–CH_2CH(CH_3)OH]^{2+}$ which decomposes *via* β-hydroxide elimination.

Introduction

There is a growing interest in the chemical properties of transient complexes with metal–carbon σ bonds in aqueous solutions due to their role in catalytic[1] and biological systems.[1–3] Such transient complexes are of major importance in a large variety of radical induced systems.[1–3] The properties of the transient complexes with chromium–carbon σ bonds are often studied as model systems due to the ease of their preparation *via*[4] reaction (1), and the relative long lifetime of the transient complexes

$$Cr(H_2O)_6^{2+} + {}^{\bullet}R \longrightarrow [(H_2O)_5Cr^{III}–R]^{2+} \qquad (1)$$

$(H_2O)_5Cr^{III}–R^{2+}$. Three main mechanisms of decomposition of these complexes were reported. (a) Heterolysis,[4,5] eqn. (2). This

$$[(H_2O)_5Cr^{III}–R]^{2+} \xrightarrow{H_2O,\ H^+} Cr(H_2O)_6^{3+} + RH \qquad (2)$$

reaction is usually acid catalysed,[4,6] *i.e.* $-d[(H_2O)_5Cr^{III}–R^{2+}]/dt = k^0[(H_2O)_5Cr^{III}–R^{2+}] + k^{H^+}[H_3O^+][(H_2O)_5Cr^{III}–R^{2+}]$, but in some systems also general base catalysed heterolysis[6,7] has been observed. (b) Homolysis,[8,9] eqn. (3). This reaction is usually

$$[(H_2O)_5Cr^{III}–R]^{2+} \longrightarrow Cr(H_2O)_6^{2+} + {}^{\bullet}R \qquad (3)$$

important[8,9] only in the absence of an excess of $Cr(H_2O)_6^{2+}$ or in the presence of a good scavenger for either the radical ${}^{\bullet}R$ or for $Cr(H_2O)_6^{2+}$. (c) β Elimination of a good leaving group,[10–14] eqn. (4) where X = OR,[15] NR_2,[16] halide,[17] *etc.* and R = H or alkyl.

$$[(H_2O)_5Cr^{III}–CR^1R^2CR^3R^4X] \longrightarrow Cr(H_2O)_6^{3+} + R^1R^2C{=}CR^3R^4 + X^- \qquad (4)$$

In one system the results indicate that a β-hydride shift contributes to the mechanism of decomposition of the transient complex,[18] eqn. (5) where L = 1,4,8,12-tetraazacyclopentadecane.

$$[L(H_2O)Cr^{III}–CH(OH)CH_3]^{2+} \longrightarrow [L(H_2O)Cr^{III}–H]^{2+} + CH_3CHO \qquad (5)$$

During a recent study on the chemical properties of the transient complex $(H_2O)_5Cr^{III}–CH_2C(O)CH_3^{2+}$, which seems to decompose *via* a heterolytic pathway,[19] it was observed that some propene is formed under conditions where $[(H_2O)_5Cr^{III}–C(CH_3)_2(OH)]^{2+}$ might be formed. It was decided therefore to reinvestigate the mechanism of decomposition of the latter complex.

Reaction (6) was studied by Taube and co-workers[20] in the

$$[(H_2O)_5Cr^{III}–C(CH_3)_2OH]^{2+} \xrightarrow{H_2O,\ H^+} Cr(H_2O)_6^{3+} + \text{products} \qquad (6)$$

presence of an excess of $Cr(H_2O)_6^{2+}$. The reaction obeys rate law (7) with $k^0 = 3.3 \times 10^{-3}\ s^{-1}$ and $k^{H^+} = 4.7 \times 10^{-3}\ dm^3\ mol^{-1}$

$$\frac{-\,d[(H_2O)_5Cr^{III}–C(CH_3)_2OH^{2+}]}{dt} = k^0[(H_2O)_5Cr^{III}–C(CH_3)_2OH^{2+}] + k^{H^+}[H_3O^+][(H_2O)_5Cr^{III}–C(CH_3)_2OH^{2+}] \qquad (7)$$

s^{-1}. It was proposed that 2-propanol is the organic product of this reaction as methanol was shown to be the product of decomposition of the transient complex $[(H_2O)_5Cr^{III}–CH_2OH]^{2+}$, a reaction which proceeds with a similar rate law, with $k^0 = 7 \times 10^{-4}\ s^{-1}$ and $k^{H^+} = 3.2 \times 10^{-4}\ dm^3\ mol^{-1}\ s^{-1}$.

The results reported herein indeed indicate that propene is a major product of the acid catalysed pathway. It is proposed that the mechanism of formation of the propene involves isomerization of $[(H_2O)_5Cr^{III}–C(CH_3)_2OH]^{2+}$ into $[(H_2O)_5Cr^{III}–CH_2CH(CH_3)(OH)]^{2+}$, *via* a β-hydride shift followed by a β elimination of OH^-.

Experimental

Materials

All solutions were prepared from AR grade chemicals and from distilled water. The latter was further purified by passing through a Milli Q Millipore set-up, final resistivity >10 MΩ cm^{-1}. Solutions of $[Cr(H_2O)_6][ClO_4]_2$ (0.35 mol dm^{-3}) were prepared by dissolving super pure chromium powder, Aldrich chemical company Inc., in 1.0 mol dm^{-3} perchloric acid solution continuously purged with helium gas. The gas was first purged from dioxygen impurities by bubbling through two washing towers containing VSO_4 in dilute H_2SO_4 over zinc amalgam. The chromium(II) concentration was established by its UV-Vis spectrum ($\varepsilon = 5.0\ dm^3\ mol^{-1}\ cm^{-1}$ at $\lambda = 712$ nm). All solutions containing chromium(II) were handled under deaerated conditions by the syringe technique. The pH was measured with a Corning 22 pH meter and adjusted by addition of $HClO_4$ and/or NaOH. All the experiments were carried out at room temperature, 22 ± 2 °C.

Preparation of $[(H_2O)_5Cr^{III}–C(CH_3)_2(OH)]^{2+}$ complex

I The "modified Fenton reagent" technique. A deaerated solution containing $Cr(H_2O)_6^{2+}$ and 2-propanol at the required pH was mixed in a bulb with a deaerated solution containing H_2O_2. Upon mixing following reactions (8)–(11) occur.[4] The concentration of the $Cr(H_2O)_6^{2+}$ ions is maintained at a >2.5-fold excess of hydrogen peroxide.

$$Cr(H_2O)_6^{2+} + H_2O_2 \longrightarrow Cr(H_2O)_6^{3+} + {}^{\bullet}OH + OH^- \quad (8)$$

$$^{\bullet}OH + CH(CH_3)_2OH \begin{array}{l} \nearrow H_2O + {}^{\bullet}C(CH_3)_2OH \quad 85.5\%^{21} \\ \searrow H_2O + {}^{\bullet}CH_2CH(CH_3)(OH) \quad 13.3\%^{21} \end{array} \quad (9)$$

$$Cr(H_2O)_6^{2+} + {}^{\bullet}C(CH_3)_2OH \longrightarrow [(H_2O)_5Cr^{III}–C(CH_3)_2OH]^{2+} \quad (10)$$

$$Cr(H_2O)_6^{2+} + {}^{\bullet}CH_2CH(CH_3)(OH) \longrightarrow [(H_2O)_5Cr^{III}–CH_2CH(CH_3)(OH)]^{2+} \quad (11)$$

II The radiolytic technique. Deaerated solutions containing $Cr(H_2O)_6^{2+}$ and 2-propanol at the required pH in a bulb were irradiated in a ^{60}Co γ source. The radiolysis of acidic solutions produces $^{\bullet}OH$ radicals, which react *via* reaction (9), followed by (10) and (11) and hydrogen atoms which react *via* eqn. (12) followed by (10) and (11).

$$H^{\bullet} + CH(CH_3)_2OH \begin{array}{l} \nearrow H_2 + {}^{\bullet}C(CH_3)_2OH \\ \quad k = 7.8 \times 10^7\ dm^3\ mol^{-1}\ s^{-1\,22} \\ \searrow H_2 + {}^{\bullet}CH_2CH(CH_3)OH \end{array} \quad (12)$$

Gas analysis

The different products were analysed by gas chromatography. Samples of the gases produced were taken from the bulb by using gas tight syringes and analysed using a Varian model 3700 gas chromatograph equipped with a thermal conductivity detector in series to a flame ionization detector. The samples were separated on a 1/8 in 10 ft long Poropack Q column. The oven temperature program for propene separation was 35 to 160 °C at 30 °C min^{-1} then held at 160 °C for 10 min. Calibration curves were obtained in order to determine quantitatively the amounts of the gases formed.

The gaseous products of deaerated solutions which contained Cr^{II}, 2-propanol and hydrogen peroxides in D_2O or water were measured using a Balzers model QMG-421 quadruple mass spectrometer equipped with a SEM (Secondary Electron Multiplier).

The % yields for the irradiated samples were calculated from the observed yields assuming that G(products) = 6.1 corresponds to a yield of 100%, where G is the number of product molecules formed per 100 eV absorbed by the solution. The % yields for the "modified Fenton reagent" were calculated relative to the initial concentration of hydrogen peroxide in the solution (4×10^{-4} mol dm^{-3}).

Results and discussion

The gaseous products produced either by mixing He saturated solutions containing 2×10^{-3} mol dm^{-3} Cr^{2+}_{aq} and 0.4 mol dm^{-3} 2-propanol with solutions containing 8×10^{-4} mol dm^{-3} H_2O_2, in the pH range 0–3, or by irradiating in the ^{60}Co γ source He saturated solutions containing 1×10^{-3} mol dm^{-3} Cr^{2+}_{aq} and 0.2 mol dm^{-3} 2-propanol were determined. The pH dependence of the product distribution is summarized in Table 1.

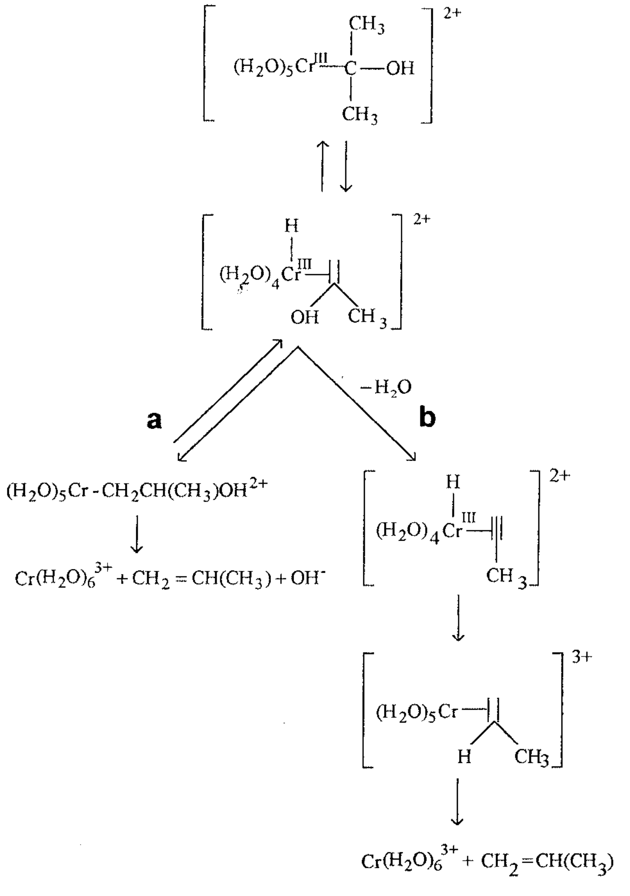
Table 1 Yields of propene produced by the decomposition reaction of the complex $[(H_2O)_5Cr–C(CH_3)_2(OH)]^{2+}$ at different pH[a]

$[H_3O^+]$/ mol dm^{-3}	Propene yield (H_2O_2) (%)	Propene yield (irradiation), G%
0.001	9.0	10.7
0.032	11.0	11.5
0.100	13.0	15.4
0.320	21.0	20.0
1.000	—	45.0

[a] The solutions contained 1×10^{-3} mol dm^{-3} Cr^{2+}_{aq} and 0.2 mol dm^{-3} 2-propanol (and additionally 4×10^{-4} mol dm^{-3} H_2O_2 for the modified Fenton reaction). Error limit ±2%.

Mass spectrometric measurements revealed that no H_2 is formed in the decomposition of $[(H_2O)_5Cr–C(CH_3)_2(OH)]^{2+}$, *i.e.* the H_2 yields are not affected by the addition of $Cr(H_2O)_6^{2+}$ to the irradiated solutions and no H_2 is formed by the "Fenton" reagent. The yield of propene at pH 3.0 is attributed to the $^{\bullet}CH_2CH(CH_3)OH$ radicals formed in reactions (9) and (12) which react with $Cr(H_2O)_6^{2+}$, eqn (11), to form the transient complex $[(H_2O)_5Cr^{III}–CH_2CHCH_3(OH)]^{2+}$ which is known to decompose into $Cr(H_2O)_6^{2+}$ and propene in an acid catalysed process.[11] The yield of propene, Table 1, clearly increases with the increase in acidity, *i.e.* the acid catalysed decomposition of $[(H_2O)_5Cr–C(CH_3)_2(OH)]^{2+}$, reaction (6), also changes the nature of the organic products. However, even at pH 0 propene is not the only organic product of decomposition of $[(H_2O)_5Cr–C(CH_3)_2(OH)]^{2+}$. The other organic product, which is not detected by the GC analysis, or in the MS of the gaseous phase, is probably 2-propanol, which was believed to be the sole product up to now.[10a,20]

Two plausible mechanisms are envisaged for the formation of propene from $[(H_2O)_5Cr–C(CH_3)_2(OH)]^{2+}$, Scheme 1: (a) *via* a



Scheme 1

Table 2 Rate constants for decomposition of the complexes $[(H_2O)_5Cr–R]^{2+}$, obeying the equation $k_{obs} = k^0 + k^{H^+}[H_3O^+]$[20]

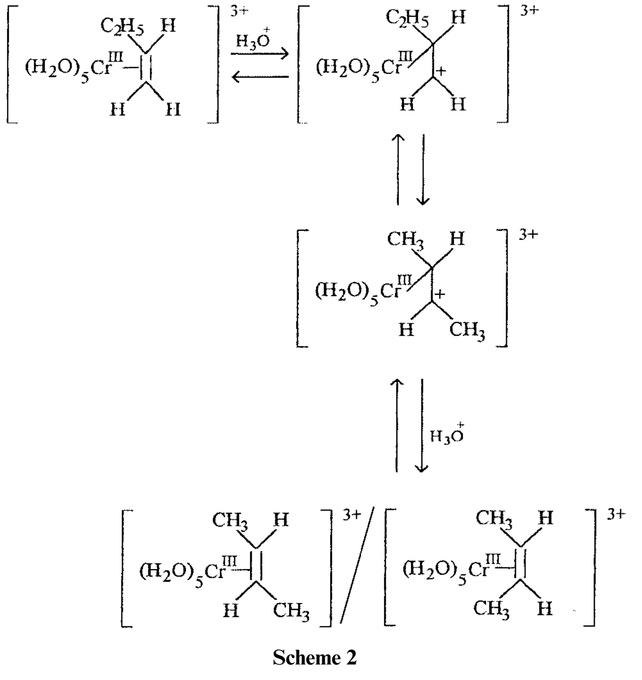
k^{H^+}/dm^3 mol^{-1} s^{-1}	k^0/s^{-1}	R
3.2×10^{-4}	7×10^{-4}	CH_2OH
1.2×10^{-3}	1.9×10^{-3}	$CH(OH)CH_3$
4.7×10^{-3}	3.3×10^{-3}	$C(CH_3)_2OH$

β-hydride shift step which induces isomerization of $[(H_2O)_5Cr–C(CH_3)_2(OH)]^{2+}$ into $[(H_2O)_5Cr–CH_2CH(CH_3)(OH)]^{2+}$ which is followed by β elimination of hydroxide; (b) *via* the same β-hydride shift step followed by a water elimination step. The product of both suggested mechanisms is propene. However if the reaction proceeds *via* mechanism (b) one of the hydrogen atoms in the product originates from the solvent. Therefore in order to distinguish between these two mechanisms the experiments were repeated in D_2O. No deuterium enrichment of the propene was observed. It has therefore to be concluded that the propene is formed *via* mechanism (a).

The results give no clue to the question, which of the steps of mechanism (a) is the acid catalysed step. Two possibilities are envisaged: I one, or both, of the equilibria involved in the mechanism are acid catalysed, due to unclear reasons; II both equilibrium constants are small, *i.e.* the concentration of $[(H_2O)_5Cr^{III}–CH_2CH(CH_3)OH]^{2+}$ is always small. The latter complex decomposes in an acid catalysed process. The rate constant of this reaction is unknown, however that of the analogous reactions for $[(H_2O)_5Cr^{III}–CH_2CH_2OH]^{2+}$ and $[(H_2O)_5Cr^{III}–CH(CH_3)CH_2OH]^{2+}$ are $(2.0 \pm 1.4) \times 10^4[H_3O^+]$ and $(2.1 \pm 1.1) \times 10^5[H_3O^+]$ s^{-1} respectively.[12] This mechanism predicts that the relative yields of propene should increase linearly with $[H_3O^+]$, as was observed, within the experimental error limit, Table 1.

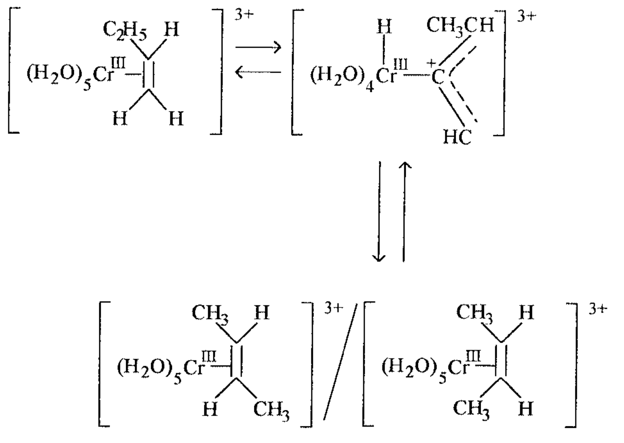
Methyl substituents accelerate the rate of decomposition of the $[(H_2O)_5Cr–CR^1R^2(OH)]^{2+}$ complexes, Table 2. The effect of the methyl substituents on k^{H^+} is clearly considerably larger than that on k^0. This difference is now attributed, at least in part, to the acid catalysed isomerization reaction (11).

It should be noted that a β-hydride shift was not observed as a major decomposition route of any of the many $[(H_2O)_5Cr^{III}–R]^{2+}$ complexes studied. This could be due to the lack of a good β-leaving group after the isomerization in these complexes. Therefore even if isomerization occurs the same organic product will be formed after heterolysis. However, if isomerization *via* a β hydride-shift mechanism occurs generally with a rate of ≈1×10^{-3} s^{-1} then the rate of heterolysis of $[(H_2O)_5Cr^{III}–CH(CH_3)_2]^{2+}$ and $[(H_2O)_5Cr^{III}–CH_2CH_2CH_3]^{2+}$ (if those rates are slower than the rate of β-hydride shift) should be identical. The reported kinetic data[4] do not confirm this expectation. It has therefore to be concluded that the α-hydroxyl substituent accelerates the rate of the β-hydride shift induced isomerization.



Scheme 2

Finally it is tempting to point out that the isomerization of the d ⟶ π complex of $(H_2O)_5Cr^{3+}$ with 1-butene into the analogous complex with 2-butene was proposed to proceed *via* the mechanism outlined in Scheme 2.[12] It seems now that a plausible alternative mechanism is Scheme 3.



Scheme 3

Acknowledgements

This study was supported in part by a grant from the Budgeting and Planning Committee of the Council of higher Education and the Israel Atomic Energy Commission. D. M. wishes to express his thanks to Mrs Irene Evens for her ongoing interest and support.

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