The atomic parameters used are summarized in Table V. Idealized experimental molecular structures were considered for isomers a and b and the dimer $[Mo(CO)_3Cp]_2$. In all the calculations, the following bond distances (Å) were used: Pt–Pt = 2.65; Mo–C (Cp) = 2.35; Mo–C (CO) = 1.98; Pt–P = 2.29; C–O = 1.15; C–C = 1.41; P–H = 1.40; and C–H = 1.09.

X-ray Data Collection and Structural Determination for 2b. Single crystals of **2b** were obtained by slow diffusion of *n*-hexane into a CH_2Cl_2 solution of the complex at −20 °C. Crystal data and intensity collection parameters are given in Table VI. Precise lattice parameters were obtained by standard Enraf-Nonius least-squares methods with use of 25 carefully selected reflections and Mo Kα radiation (graphite monochromator, $\lambda = 0.71073$ Å). No intensity decay was observed during the data collection periods. Intensity data were collected on an Enraf-Nonius-CAD4 diffractometer, and for all subsequent computations, the Enraf-Nonius SDP package was used.[57] Intensities were corrected for Lorentz and polarization factors except that absorption corrections were omitted. The crystal structures were solved by using the MULTAN program and Fourier methods in the space group $P2_1/n$, assumed on the basis of an $N(z)$ cumulative test on $|F_o|$.[58] Crystal data for $[Pt_2Mo_2Cp'_2(CO)_6(PCy_3)_2]$ (**2b**): $C_{54}H_{80}Mo_2O_6P_2Pt_2$, $M_W = 1469.25$; monoclinic, $P2_1/n$; crystal dimensions, 0.40 × 0.15 × 0.15 mm; $a = 10.321$ (3), $b = 24.351$ (8), $c = 21.368$ (6) Å; $\beta = 92.76$ (4)°; $V = 5364$ Å^3; $Z = 4$; $F(000) = 2888e$; $d_{calcd} = 1.819$ g·cm^{-3}; 25 °C; $\mu = 58.05$ cm^{-1}; $\pm h$, $+k$, $+l$ octants collected; θ–2θ scan to a maximum θ of 25° and a minimum θ of 1°, giving 7840 unique reflections of which 5679 were used according to the criterion that $I > 3\sigma(I)$. Hydrogen atoms were introduced by their computed coordinates (C–H 0.95 Å) in structure factor calculations with isotropic thermal parameters of 4.0 Å^2 but were not refined. Full least-squares refinements minimizing the function $\sum(|F_o| - |F_c|)^2$ converged to a final $R = \sum||F_o| - |F_c||/\sum|F_o|$ value of 0.042, an $R_w = [\sum_w(|F_o| - |F_c|)^2/\sum_w|F_o|^2]^{1/2}$ value of 0.052 with a (goodness of fit) GOF $= [\sum_w(|F_o| - |F_c|)^2/(\text{number of reflections} - \text{number of parameters})]^{1/2}$ of 1.52. Each reflection was weighted by using $\sigma^2(F_0) = \sigma^2_{counts} + (pI)^2$. A final difference map revealed no significant residual peaks. The neutral atom scattering factors used for all atoms and anomalous dispersion coefficients were obtained from standard sources.[59] Final positional parameters with their estimated standard deviations corresponding to the final least-squares refinement cycles are given in the supplementary material (Table S-I).

Acknowledgment. We are grateful to the CNRS for financial support and to the Johnson Matthey Technology Center for a generous loan of K_2PtCl_4.

Supplementary Material Available: Tables of positional parameters (Table S-I), calculated hydrogen atom coordinates (Table S-II), complete bond lengths and angles (Tables S-III and S-IV), anisotropic thermal parameters (Table S-V) used in the refinement for **2b** (11 pages); listing of the observed and calculated structure factor amplitudes used in the refinement (Table S-VI) for **2b** (29 pages). Ordering information is given on any current masthead page.

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Stereospecificity of the β-Hydroxyl Elimination from the (Hydroxyalkyl)chromium Complex $(H_2O)_5Cr^{III}\text{-}CH(CH_3)CH(CH_3)OH^{2+}$

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Contribution from the Nuclear Research Centre Negev, Beer-Sheva, Israel, and R. Bloch Coal Research Center and Chemistry Department, Ben Gurion University of the Negev, Beer-Sheva, Israel. *Received July 24, 1990*

Abstract: The reaction of the aliphatic free radical $^{\bullet}CH(CH_3)CH(OH)CH_3$ (formed by $^{\bullet}OH$ addition to *cis*-/*trans*-2-butene or by hydrogen abstraction from 2-butanol by $^{\bullet}OH$ free radicals) with chromous ions in aqueous solutions was investigated. The radical reacts with $Cr^{2+}(aq)$, $k = 1.1 \times 10^8$ M^{-1} s^{-1}, to yield a transient complex with a chromium–carbon σ bond. The transient complex decomposes via an acid-catalyzed β-elimination reaction, $k = (230 + 9.8 \times 10^4[H_3O^+])$ s^{-1}, to form a complex in which the tervalent chromium is bound to 2-butene by a $d \rightarrow \pi$ bond. This complex decomposes to produce *cis*- or *trans*-2-butene. At pH >2 *cis*- and *trans*-2–butene are produced in equal amounts whereas in acidic solutions, pH <1, the thermodynamically less stable *cis*-2-butene is produced in considerable excess. These results are discussed and tentatively explained by the higher rate of dissociation of the cis $d \rightarrow \pi$ complex coupled with an acid-catalyzed isomerization of the two $d \rightarrow \pi$ complexes. The rate of the hydrolysis of the chromium $d \rightarrow \pi$ complex obeys the rate law $k = (0.8 + 6.7[H_3O^+])$ s^{-1}. The same mechanism also explains the effect of pH on the relative yields of 1-butene and 2-butene obtained in the oxidation of 2-butanol by $Cr^{2+}(aq)$ and H_2O_2. The rates of the β-elimination reactions of $(H_2O)_5Cr^{III}\text{–}CH_2CH_2OH^{2+}$ and $(H_2O)_5Cr^{III}\text{–}CH(CH_3)CH_2OH^{2+}$ are also reported; the results indicate that methyl substituents considerably affect the rate of β-elimination reactions.

Introduction

There is a growing interest in the chemistry of complexes with metal–carbon σ bonds in aqueous solutions. This interest stems from the realization that such complexes, which are usually unstable species, play a key role in a variety of important processes. These include the following: (a) biological processes, e.g. reactions catalyzed by vitamin B_{12},[2] oxidations by cytochrome P-450,[3] and reductive desulfurization of a methyl thioether to methane through $L^1Ni^{II}\text{–}CH_3$ (L^1 = tetrahydrocorphin) followed by protonolysis;[4]

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(1) (a) Nuclear Research Centre Negev. (b) R. Bloch Coal Research Center, Ben-Gurion University of the Negev. (c) Chemistry Department, Ben-Gurion University of the Negev.

(2) (a) Halpern, J. *Acc. Chem. Res.* **1982**, *15*, 238. (b) Halpern, J. *Pure Appl. Chem.* **1979**, *51*, 2171. (c) Scheffold, R. *Chimia* **1985**, *39*, 203. (d) Halpern, J. *Pure Appl. Chem.* **1983**, *55*, 1059. (e) Babior, B. M. *Acc. Chem. Res.* **1975**, *8*, 376. (f) Abeles, R. H.; Dolphin, D. *Acc. Chem. Res.* **1976**, *9*, 114. (g) Schrauzer, G. N. *Angew. Chem., Int. Ed. Engl.* **1977**, *16*, 233. (h) Finke, R. G.; Schiraldi, D. A.; Mayer, B. *Coord. Chem. Rev.* **1984**, *54*, 1. (i) Bresciani-Pahor, N.; Foriolin, M.; Marzilli, L. G.; Randaccio, L.; Summers, M. F.; Toscano, P. *Coord. Chem. Rev.* **1985**, *63*, 1.

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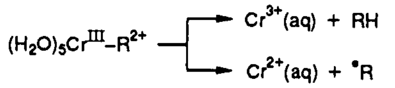
(b) radiation-induced damage to biological systems, e.g. DNA, RNA, enzymes, etc.;[5] (c) catalytic processes involving free radicals, e.g. oxidations by Fenton's reagent;[6] (d) industrial processes that are carried out in aprotic media.

The chemical properties of complexes with chromium–carbon σ bonds in aqueous solutions have been extensively studied.[7] These complexes are relatively easy to synthesize via the reaction of aliphatic free radicals with Cr(II) complexes and are relatively stable.[7] Therefore, these complexes are considered to be good model compounds for the study of the chemical properties of complexes with metal–carbon σ bonds in aqueous solutions.

The common mechanism of decomposition of complexes with a chromium–carbon σ bond in aqueous solutions involves either heterolytic or homolytic cleavage of the Cr–C bond, reaction 1.[7]

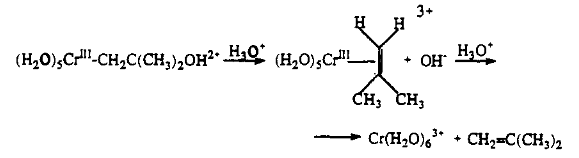


$$(H_2O)_5Cr^{III}\text{–}R^{2+} \rightarrow Cr^{3+}(aq) + RH \quad (1a)$$
$$(H_2O)_5Cr^{III}\text{–}R^{2+} \rightarrow Cr^{2+}(aq) + {}^{\bullet}R \quad (1b)$$

It has been noted that when the aliphatic residue contains a readily dissociable functional group on the β-carbon atom, relative to the chromium, the complexes decompose via a β-elimination process, reaction 2, to yield an alkene and a tervalent chromium complex as the final stable products.[7]

$$(H_2O)_5Cr^{III}\text{—}CR^1R^2CR^3R^4X^{2+} \rightarrow Cr^{3+}(aq) + R^1R^2C{=}CR^3R^4 + X^- \quad (2)$$

Reports on such processes for halides (chloride, bromide, and iodide), hydroxyls, and ether groups in aqueous, mixed, and organic solvents showed that the reactions are solvent and pH dependent.[8] For hydroxyl groups, such reactions were also observed for Cu^{II},[9] Cu^{III},[10] Co^{III},[11] and Fe^{III}[12] systems. Recently, we have shown[13] that the mechanism of the decomposition of the $(H_2O)_5Cr\text{–}CH_2C(CH_3)_2OH^{2+}$ (formed by the reaction of the aliphatic free radical ${}^{\bullet}CH_2C(CH_3)_2OH$ with chromous ions) involves the formation of a chromium(III) d→π complex which hydrolyzes to the corresponding alkene and tervalent chromium; via reaction 3.



$$(H_2O)_5Cr^{III}\text{-}CH_2C(CH_3)_2OH^{2+} \xrightarrow{H_3O^+} (H_2O)_5Cr^{III}\text{—}(\pi\text{-}CH_2{=}C(CH_3)_2)^{3+} + OH^- \xrightarrow{H_3O^+} Cr(H_2O)_6^{3+} + CH_2{=}C(CH_3)_2 \quad (3)$$

In the 1960s, the groups of Castro[8a,b] and Kochi[8c,d] published a series of reports in which observations of β-elimination reactions of different chromium–carbon complexes with β functional groups were given. Singelton and Kochi[14] reported stereospecifity for the β elimination with $Cr\text{–}CH(CH_3)CH(CH_3)Br^{2+}$ favoring the cis product only with DMSO as solvent (>90%) whereas in DMF and ethanol the thermodynamically favored *trans*-2-butene was produced in excess. These studies were performed with relatively high concentrations of chromous ions, and no yields were measured, only the product distribution.

We decided to study in detail the reaction of the β-hydroxy radical ${}^{\bullet}CH(CH_3)CH(CH_3)OH$ with chromous ions in aqueous solutions in order to shed some light on the stereospecifity of the β-elimination process. Indeed, the results indicate that the reaction has stereospecificity favoring the thermodynamically unstable *cis*-2-butene under some conditions.

Experimental Section

Materials. All solutions were prepared from AR grade chemicals that were used without further treatment and from distilled water that was further purified by passing through a Millipore Q setup so that its final resistance was >10 MΩ/cm. Research grade *cis*-2-butene, *trans*-2-butene, and 1-butene were supplied in lecture bottles by Phillips 66.

Chromous perchlorate solutions (0.5 M) were prepared by dissolving Superpure (BDH) chromium powder in 1.0 M perchloric acid solutions continuously purged with helium gas. The gas was first purged of dioxygen impurities by being bubbled through two washing bottles containing VSO_4 in dilute H_2SO_4 over zinc amalgam. The 0.5 M $Cr(H_2O)_6(ClO_4)_2$ solution thus obtained was diluted and mixed with other reagents as required. All solutions containing chromous ions were handled under deaerated conditions by using syringe techniques.

The degree of labeling of the butenes by deuterium, when the experiments were carried out in D_2O, was determined by using a Balzers quadrupole mass spectrometer, Model QMG 511.

Gas Analysis. The different alkenes were analyzed by gas chromatography and separated on a 6 in. × $^1/_4$ in. stainless steel column packed with Poropak Q coated with isobutyl vinyl ether at 33 °C, the retention times being 4.2, 5.2, and 6.5 min (at 30 mL/min flow of He) for 1-butene, *trans*-2-butene, and *cis*-2-butene, respectively. The analysis was performed by using a TCD-equipped Varian Model 3700 gas chromatograph. Calibration curves were obtained in order to determine quantitatively the amounts of the gases formed.

The Modified Fenton Reagent Technique. This technique was used for production of relatively high concentrations of the alkenes that could not be produced by the irradiations (see below). A deaerated solution containing chromous ions and 2-butanol at the required pH was mixed in a bulb with a deaerated H_2O_2 solution. Upon mixing, the following reactions occur:

$$Cr(H_2O)_6^{2+} + H_2O_2 + H_3O^+ \rightarrow Cr(H_2O)_6^{3+} + {}^{\bullet}OH^{15} \quad (4)$$

$${}^{\bullet}OH + \text{2-butanol} \rightarrow {}^{\bullet}R + H_2O \qquad k = 3.1 \times 10^9\ M^{-1}\ s^{-1\,16} \quad (5)$$

$${}^{\bullet}R + Cr(H_2O)_6^{2+} \rightarrow (H_2O)_5Cr^{III}\text{–}R^{2+\,7} \quad (6)$$

The species ${}^{\bullet}R$ is in fact a mixture of four aliphatic radicals,[17] as the production of the radicals occurs via hydrogen abstraction by the ${}^{\bullet}OH$ radicals. Thus, ${}^{\bullet}CH(CH_3)CH(CH_3)OH$, ${}^{\bullet}CH_2CH(OH)CH_2CH_3$, ${}^{\bullet}CH_2CH_2CH(CH_3)OH$, and ${}^{\bullet}C(CH_3)(CH_3CH_2)OH$ are produced. The α-carbon (relative to the hydroxyl) is most susceptible to the H abstraction process; thus, ${}^{\bullet}C(CH_3)(CH_3CH_2)OH$ is the major radical produced. The second expected point of abstraction is from the other nonterminal carbon, producing the β radical ${}^{\bullet}CH(CH_3)CH(CH_3)OH$.[17] The yield of the other two radicals is very low.[17] The 2-butanol/chromous ion/hydrogen peroxide ratio is controlled so that the oxidation of chromous ions by hydroxyl radicals, reaction 7, does not compete with reaction 5.

$${}^{\bullet}OH + Cr(H_2O)_6^{2+} + H_3O^+ \rightarrow Cr(H_2O)_6^{3+} \qquad k = 4.8 \times 10^9\ M^{-1}\ s^{-1\,16} \quad (7)$$

The concentration of chromous ions is maintained >2.5-fold in excess of hydrogen peroxide. Samples of the gases produced were taken from the bulb by using gastight syringes and analyzed in the gas chromatograph.

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Pulse Radiolysis Technique. This technique was used to measure the specific rates of reaction of the formation and decomposition of different chromium complexes with relatively short lifetimes and also to determine the UV–vis absorption spectra of the intermediates formed in the reactions studied.

Short electron pulses from the electron linear accelerator at the Hebrew University of Jerusalem were used. The dose per pulse was in the range 5×10^2–3×10^3 rd/pulse. The kinetics of the formation and decomposition of the unstable species formed by the electron pulse were followed spectrophotometrically. The experimental techniques used throughout this study and the experimental setup have been described earlier in detail.[7b]

The radiolysis of water in dilute aqueous solutions can be summarized by[18]

$$H_2O \xrightarrow{\gamma,\, e^-} e_{aq}^-,\ {}^{\bullet}H,\ {}^{\bullet}OH,\ H_2,\ H_2O_2,\ H_3O^+ \tag{8}$$

The yields of these products are[18] $G_{e_{aq}^-} = 2.65$, $G_{OH} = 2.65$, $G_H = 0.60$, $G_{H_2} = 0.45$, and $G_{H_2O_2} = 0.75$ (G value is defined as the number of molecules of each product/100 eV radiation absorbed in the solution). In concentrated solutions, the yields of the primary free radicals are often somewhat higher and those of dihydrogen peroxide are somewhat lower.[18]

In neutral N_2O-saturated (0.022 M) solutions that also contain either *cis*- or *trans*-2-butene, reactions 9 and 10 occur. Under the experimental

$$N_2O + e_{aq}^- + H_3O^+ \rightarrow N_2 + H_2O + {}^{\bullet}OH \qquad k = 8.7 \times 10^9\ M^{-1}\ s^{-1}\ {}^{16} \tag{9}$$

$$ {}^{\bullet}OH + cis\text{-}/trans\text{-}2\text{-butene} \rightarrow {}^{\bullet}CH(CH_3)CH(CH_3)OH \qquad k > 5 \times 10^9\ M^{-1}\ s^{-1}\ {}^{16} \tag{10}$$

conditions (90% *cis*-/*trans*-2-butene saturation, $(2–5) \times 10^{-3}$ M, and 10% N_2O saturation, 2.2×10^{-3} M) all the hydroxyl radicals and the hydrated electrons are transformed within 5 μs from the pulse into ${}^{\bullet}CH(CH_3)CH(CH_3)OH$ radicals.

Irradiations in a γ Source. Steady-state irradiations in a ^{60}Co γ source (Noratom) were carried out in bulbs, as in the Fenton reaction. However, in these experiments no hydrogen peroxide was added to the samples. The dose rate of the source was 4.5×10^3 rd/min and was determined by using the Fricke dosimeter.[18]

pH Determinations. Determination of the pH's in the range 1.0–4.7 was carried out under deaerated conditions while helium was bubbled through the syringe or the bulb in which the measurement was performed. The measurement was taken immediately after the irradiation in order to prevent pH changes due to the oxidation of chromous ions by air. The pH's below pH 1.0 are values calculated from the concentrations of $HClO_4$ added to the sample.

Results

Solutions containing $(1–20) \times 10^{-4}$ M $Cr^{2+}(aq)$ in the pH range 0–5 and saturated with 10–90% *cis*-/*trans*-2-butene and 90–10% N_2O, respectively, were irradiated by a short electron pulse from the linear accelerator. The formation of an intermediate with absorption bands similar to those of other complexes with a chromium–carbon σ bond in aqueous solutions[7] was observed. The results are independent of the nature of the 2-butene used, i.e. *cis*- or *trans*-2-butene. The spectrum of the intermediate is plotted in Figure 1A. It has two absorption maxima at $\lambda^1_{max} = 280 \pm 5$ nm ($\epsilon^1_{max} = 2600 \pm 400\ M^{-1}\ cm^{-1}$) and $\lambda^2_{max} = 400 \pm 5$ nm ($\epsilon^2_{max} = 450 \pm 70\ M^{-1}\ cm^{-1}$). The formation of the transient occurs in the 400-μs time scale and obeys a pseudo-first-order rate law. The rate depends linearly on $[Cr^{2+}(aq)]$ and is independent of [2-butene], pH, $[N_2O]$, pulse intensity, and wavelength. The specific rate of the formation of the transient, reaction 11, was

$$ {}^{\bullet}CH(CH_3)CH(CH_3)OH + Cr(H_2O)_6^{2+} \rightarrow (H_2O)_5Cr^{III}\text{–}CH(CH_3)CH(CH_3)OH^{2+} \tag{11}$$

determined to be $k_{11} = (1.1 \pm 0.1) \times 10^8\ M^{-1}\ s^{-1}$. The transient complex $(H_2O)_5Cr^{III}\text{–}CH(CH_3)CH(CH_3)OH^{2+}$ decomposes in a process that yields a second unstable intermediate. (At pH 3 this reaction occurs within 20 ms.) The spectrum of the second intermediate is plotted in Figure 1B. It has one absorption maximum at $\lambda_{max} = 280 \pm 5$ nm ($\epsilon_{max} = 1400 \pm 200\ M^{-1}\ cm^{-1}$).

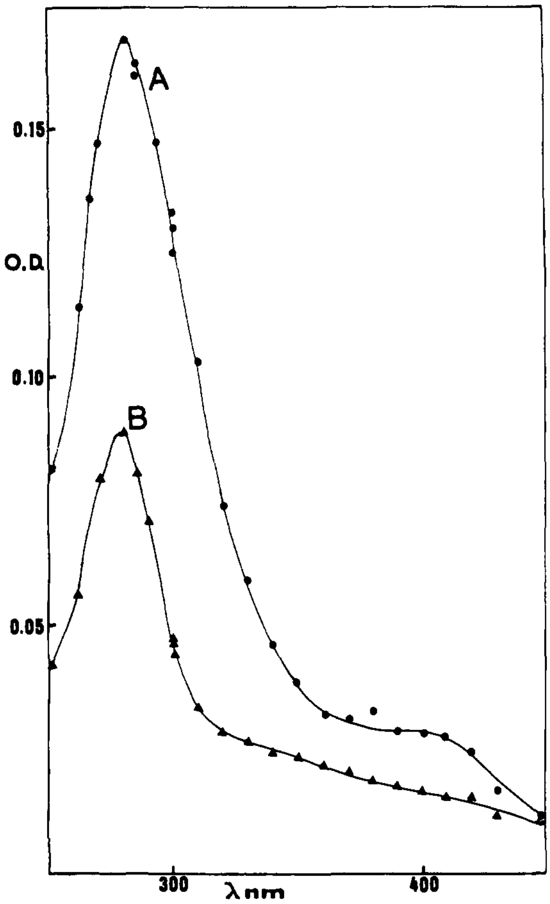

Figure 1. UV–vis spectra of the transients formed in solutions containing 2×10^{-4} M $Cr^{2+}(aq)$ at pH 3.5, 90% saturation by *cis*-2-butene and 10% by N_2O, irradiated by a short electron pulse: (A) spectrum of $(H_2O)_5CrCH(CH_3)CH(CH_3)OH^{2+}$ (intermediate I) measured 40 μs after the pulse; (B) spectrum of $(H_2O)_5Cr\{CH(CH_3){=}CH(CH_3)\}^{3+}$ (intermediate II).

The kinetics of this reaction obey a first-order rate law, the rate being independent of [2-butene], $[N_2O]$, $[Cr^{2+}(aq)]$, pulse intensity, and wavelength. However, the rate of this reaction depends linearly on the acid concentration (Figure 2A).

$$(H_2O)_5Cr^{III}\text{–}CH(CH_3)CH(CH_3)OH^{2+} + H_3O^+ \rightarrow \text{intermediate II} \tag{12}$$

Intermediate II is identified later; see Discussion. The observed rate obeys eq I.

$$k_{ob} = \{(2.3 \pm 0.5) \times 10^2 + (9.8 \pm 1.0) \times 10^4[H_3O^+]\}\ s^{-1} \tag{I}$$

The second intermediate, or mixture of intermediates, decomposes within several seconds (in the pH range 1–5) to yield stable products that have no appreciable absorption in the range 260–700 nm. The rate of this process obeys a first-order rate law, $k = 0.8 \pm 0.2\ s^{-1}$, independent of [2-butene], $[N_2O]$, and $[H^+]$ in the pH range 1–5, wavelength, and pulse intensity. However, at pH <1 an increase in the rate is observed (Figure 2b). Three typical oscillogram traces showing the three processes observed (upon irradiation with a short electron pulse from the linear accelerator) are shown in Figure 3.

The final products of the reaction were determined either by using the modified Fenton reagent (see above) in solutions containing 2×10^{-3} M H_2O_2, 5×10^{-3} M $Cr^{2+}(aq)$, and 1 M 2-butanol in the pH range 0–3 saturated with helium or in nitrous oxide saturated solutions containing 2×10^{-3} M $Cr^{2+}(aq)$ and 1 M 2-butanol irradiated for 30 min in the ^{60}Co γ source.

Three gaseous products were observed, 1-butene, *cis*-2-butene, and *trans*-2-butene. The ratio between these gases was independent of the concentrations of 2-butanol, $Cr^{2+}(aq)$, and H_2O_2 and the duration of irradiation in the γ source but was pH de-

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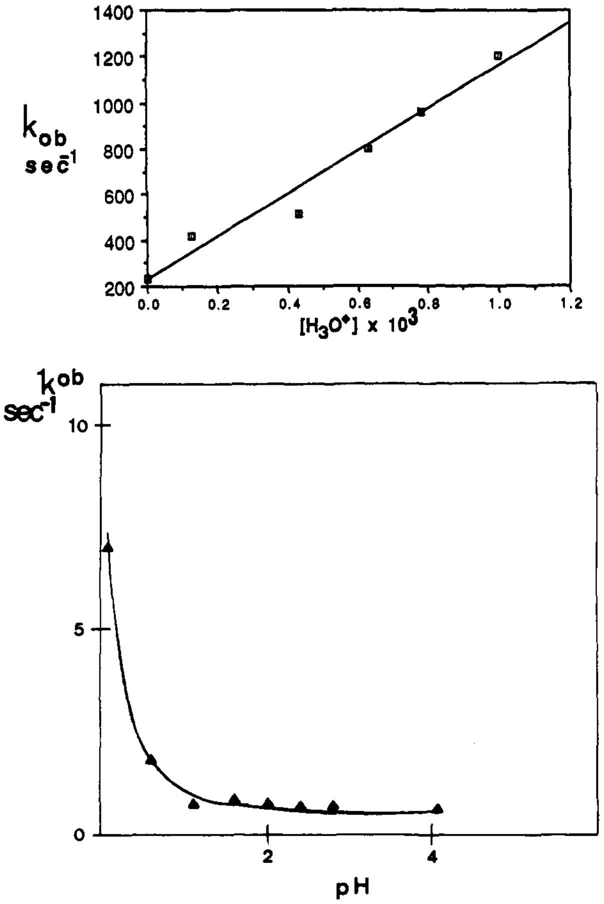


Figure 2. (a) Top: Acid dependence of the rate of decomposition of $(H_2O)_5CrCH(CH_3)CH(CH_3)OH^{2+}$ (intermediate I). (b) Bottom: pH dependence of the rate of hydrolysis of $(H_2O)_5Cr\{CH(CH_3){=}CH(CH_3)\}^{3+}$ (intermediate II) measured at 300 nm. The solutions were 90% saturated with *trans*-2-butene and 10% saturated with nitrous oxide and contained 3×10^{-4} M Cr^{2+}(aq).

pendent. In Table I the pH dependence of the product distribution is summarized. Upon addition of acetate buffer to the modified Fenton reagent at pH 2.8 and 3.8, no change in the product distribution of the alkenes is observed. In a blank experiment, *cis*-2-butene was injected into bulbs containing all the reaction components but H_2O_2 at pH 3 and 0. The gas phase was analyzed after 24 h, and only *cis*-2-butene was detected; this experiment proves that the butenes formed do not isomerize under the experimental conditions.

N_2O-saturated samples containing 2-butanol and Cr^{2+}(aq) in D_2O at pH 3.0 and 0.0 were irradiated, and the butenes formed were analyzed mass spectrometrically. The results pointed out that less than 4% of the butenes formed contain deuterium above natural abundance. This result points out that the reactions leading to the formation of the butenes do not involve protons from the solvent.

Table I.[a] Relative Yields of Alkenes Produced in the Reaction Mixture of Cr^{2+}(aq), H_2O_2, and 2-Butanol

	yield, %			
pH	1-butene	*cis*-2-butene	*trans*-2-butene	*cis*-2-butene (or total 2-butenes)
0	8.5	73.2	18.3	80
0.2	10	58.5	31.5	65
0.4	13	58.3	28.7	67
0.6	13	56.6	30.4	65
0.8	15	51.0	34.0	60
1.0	17	46.5	36.5	56
1.1	17	49.0	34.0	59
1.4	16	47.0	37.0	56
1.6	16	48.7	35.3	58
1.8	21	42.0	37.0	53
2.0	18	44.0	38.0	54
2.2	17	45.7	37.3	55
2.4	17	44.0	39.0	53
2.7	18	43.5	38.5	53
3.0	18	43.5	38.5	53
3.5	17	44.9	38.0	54
3.8	18	42.0	40.0	51
3.8[b]	18	41.0	41.0	50

[a] The solutions contained 1 M *sec*-butyl alcohol, 2×10^{-3} M H_2O_2, and 5.0×10^{-3} M Cr^{2+}(aq). [b] The solutions also contained 1×10^{-3} M acetate buffer.

Solutions containing $(1{-}30) \times 10^{-4}$ Cr^{2+}(aq) in the pH range 0–5 and saturated with 10–90% ethylene or propylene and 90–10% N_2O, respectively, were irradiated by a short electron pulse from the linear accelerator. The formation of intermediates with absorption bands typical of those for complexes with chromium–carbon σ bonds in aqueous solutions[7] was observed. The spectrum of the intermediate formed in the propylene-containing system is plotted in Figure 4. Both intermediates have two absorption bands in the near-UV region with $\lambda^1_{max} < 280$ nm ($\epsilon^1_{max} > 2600 \pm 400$ $M^{-1}\,cm^{-1}$) and $\lambda^2_{max} = 390 \pm 5$ nm ($\epsilon^2_{max} = 380 \pm 70$ $M^{-1}\,cm^{-1}$) for $(H_2O)_5Cr{-}CH_2CH_2OH^{2+}$ and $\lambda^1_{max} = 285 \pm 10$ nm ($\epsilon^1_{max} = 2100 \pm 400$ $M^{-1}\,cm^{-1}$) and $\lambda^2_{max} = 390 \pm 5$ nm ($\epsilon^2_{max} = 310 \pm 70$ $M^{-1}\,cm^{-1}$) for the intermediate formed in the propylene-saturated solutions. The kinetics of formation of the transients were observed in the 400-μs time scale and obeyed a pseudo-first-order rate law linearly dependent on $[Cr^{2+}(aq)]$ and independent of [alkene], pH, $[N_2O]$, pulse intensity, and wavelength. The specific rates of the formation of the intermediate complexes with the chromium–carbon σ bonds, reaction 13, was

$$\begin{aligned} {}^{\bullet}CH_2CH_2OH \text{ or } {}^{\bullet}CH(CH_3)CH_2OH + Cr(H_2O)_6^{2+} &\rightarrow \\ (H_2O)_5Cr^{III}{-}CH_2CH_2OH^{2+} &\text{ or } \\ (H_2O)_5Cr^{III}{-}CH(CH_3)CH_2OH^{2+} & \quad (13a,b) \end{aligned}$$

determined to be $k_{13} = (1.8 \pm 0.2) \times 10^8$ and $(1.5 \pm 0.2) \times 10^8$

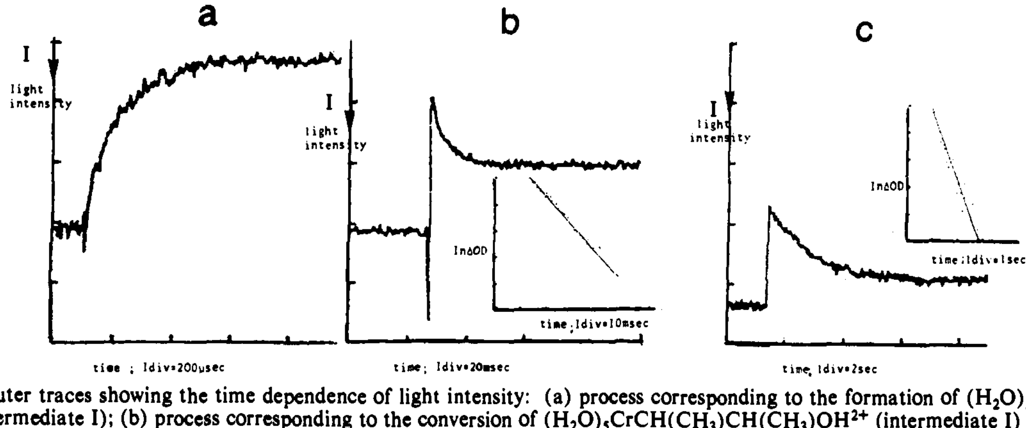


Figure 3. Computer traces showing the time dependence of light intensity: (a) process corresponding to the formation of $(H_2O)_5CrCH(CH_3)CH(CH_3)OH^{2+}$ (intermediate I); (b) process corresponding to the conversion of $(H_2O)_5CrCH(CH_3)CH(CH_3)OH^{2+}$ (intermediate I) to $(H_2O)_5Cr\{CH(CH_3){=}CH(CH_3)\}^{3+}$ (intermediate II); (c) process corresponding to the hydrolysis of $(H_2O)_5Cr\{CH(CH_3){=}CH(CH_3)\}^{3+}$ (intermediate II) (measured at 300 nm; pulse intensity 1000 rd. The solution was saturated with 90% *trans*-2-butene and 10% nitrous oxide and contained 2×10^{-4} M Cr^{2+}.

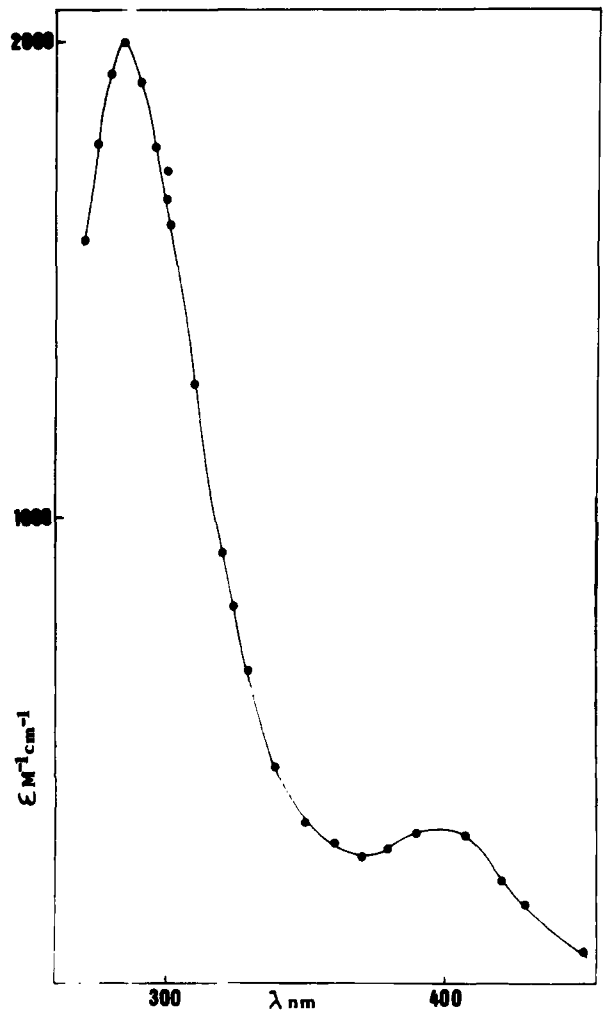
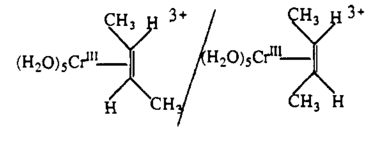


Figure 4. Spectrum of $(H_2O)_5CrCH(CH_3)CH_2OH^{2+}$. Solution composition: 1×10^{-3} M $Cr^{2+}(aq)$, pH 3.5, 40% propylene, 60% N_2O saturated.

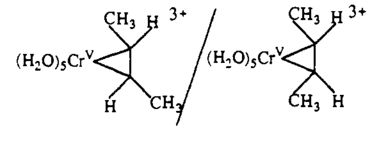
$M^{-1}\,s^{-1}$ for ethylene- and propylene-saturated solutions, respectively. The transient $(H_2O)_5Cr^{III}{-}CH_2CH_2OH^{2+}$ has been prepared earlier by a photochemical technique.[19] It decomposes to final products that do not absorb light appreciably in the UV-vis range. The rate of the decomposition reaction is independent of [ethylene], $[Cr^{2+}(aq)]$, $[N_2O]$, pulse intensity, and wavelength but is pH dependent and obeys the equation $k_d = \{(2.3 \pm 0.3) + (1.4 \pm 0.1) \times 10^4[H_3O^+]\}\ s^{-1}$. The decomposition of the transient in the propylene-saturated solutions obeys a similar rate law with $k_d = \{(2.1 \pm 0.2) \times 10 + (1.1 \pm 0.1) \times 10^5[H_3O^+]\}\ s^{-1}$. The rates of the decomposition reactions of these transients are independent of acetate buffer concentration at pH 4–5 and of ionic strength ($NaClO_4$ in the range 0.05–1 M). It should be pointed out that in these systems no second unstable intermediate is observed.

Discussion

Identification of the Intermediates. The formation of the first transient in the *cis-/trans-*2-butene-containing solutions obeys a first-order rate law both in $^\bullet CH(CH_3)CH(CH_3)OH$ and in $Cr(H_2O)_6^{2+}$. The formation of the aliphatic radical $^\bullet CH(CH_3)CH(CH_3)OH$ via reaction 10 is over in less than 5 μs, therefore, the process observed during the first 400 μs is attributed to the formation of $(H_2O)_5Cr^{III}{-}CH(CH_3)CH(CH_3)OH^{2+}$ via reaction 11. Furthermore, the UV–vis absorption spectrum of the transient resembles that of other α- and β-hydroxyalkyl Cr(III) complexes: $(H_2O)_5Cr^{III}CH(OH)CH_3^{2+}$, $\lambda^1_{max} = 296$ nm ($\epsilon^1_{max} = 2800\ M^{-1}\,cm^{-1}$), $\lambda^2_{max} = 396$ nm ($\epsilon^2_{max} = 570\ M^{-1}\,cm^{-1}$); $(H_2O)_5Cr^{III}CH_2C(CH_3)_2OH^{2+}$, $\lambda^1_{max} < 270$ nm ($\epsilon^1_{max} > 2100\ M^{-1}\,cm^{-1}$), $\lambda^2_{max} = 410$ nm ($\epsilon^2_{max} > 170\ M^{-1}\,cm^{-1}$).[7b] The intermediate $(H_2O)_5Cr^{III}{-}CH(CH_3)CH(CH_3)OH^{2+}$ decomposes to form a second unstable product, intermediate II, which has an absorption spectrum with one maximum at 280 nm and a molar extinction coefficient of 1400 $M^{-1}\,cm^{-1}$ and a broad shoulder in the near-UV region. As discussed above,[7,13] all the (β-hydroxylalkyl)pentaaaquachromium(III) complexes reported so far undergo fast β-elimination process, the rate of which is pH dependent but independent of wavelength and chromous ion or nitrous oxide concentrations, as is observed for the decomposition of $(H_2O)_5Cr^{III}{-}CH(CH_3)CH(CH_3)OH^{2+}$. Furthermore, the spectrum of intermediate II is similar to that of $(H_2O)_5Cr^{III}\{CH_2{=}C(CH_3)_2]^{3+}$.[7b,13] Therefore, it is suggested that intermediate II is a mixture of the pentaaquochromium π complexes



The later intermediates are isoelectronic with the metallacycles



The actual structure of intermediate II is somewhere between these two extreme descriptions. For brevity in the following text only the π-complex structure is used.

In ethylene-saturated solutions, the hydroxyl radicals are transformed into β-hydroxyethyl radicals in less than 1 μs via

$$^\bullet OH + CH_2{=}CH_2 \rightarrow {}^\bullet CH_2CH_2OH^{16} \qquad (14)$$

and the formation of the complex with the chromium–carbon σ bond in the 0.2-ms time range is due to the reaction of the β-hydroxyethyl radical with chromous ions, reaction 13a, $k_{13a} = 1.8 \times 10^8\ M^{-1}\,s^{-1}$. The spectrum of $(H_2O)_5Cr^{III}{-}CH_2CH_2OH^{2+}$ is indeed identical with its reported spectrum.[19] It decomposes via a β-elimination process, reaction 15, with a rate obeying the

$$(H_2O)_5Cr^{III}{-}CH_2CH_2OH^{2+} \xrightarrow{H_3O^+} CH_2{=}CH_2 + Cr(H_2O)_6^{3+} \qquad (15)$$

equation $k_{15} = (2.0 + 1.4 \times 10^4[H_3O^+])\ s^{-1}$. The value of the acid-independent term is lower than that reported by the photochemical method;[19] this discrepancy is probably due to the fact that the photochemical study was carried out in relatively acidic solutions, pH <2, and therefore, the determination of the intercept is less accurate.

In propylene-saturated solutions only one OH adduct is formed, via reaction 16.[16,20] This reaction is over in less than 1 μs under

$$^\bullet OH + CH(CH_3){=}CH_2 \rightarrow {}^\bullet CH(CH_3)CH_2OH \qquad (16)$$

the experimental conditions. Thus, the transient that is formed in the 0.2-ms time scale is the pentaaquachromium complex $(H_2O)_5Cr^{III}{-}CH(CH_3)CH_2OH^{2+}$ (reaction 13b). The absorption spectrum of this transient in the UV–vis region, Figure 5, is similar to those observed for the analogous complexes. This unstable species undergoes a β-elimination reaction, the rate of which is pH dependent, and like the corresponding $(H_2O)_5Cr^{III}{-}CH_2CH_2OH^{2+}$ decomposes to the final products propylene and tervalent chromium ions, with a rate of $k_{17} = (21 + 1.1 \times 10^5[H_3O^+])\ s^{-1}$.

$$(H_2O)_5Cr^{III}{-}CH(CH_3)CH_2OH^{2+} \xrightarrow{H_3O^+} CH_3CH{=}CH_2 + Cr(H_2O)_6^{3+} \qquad (17)$$

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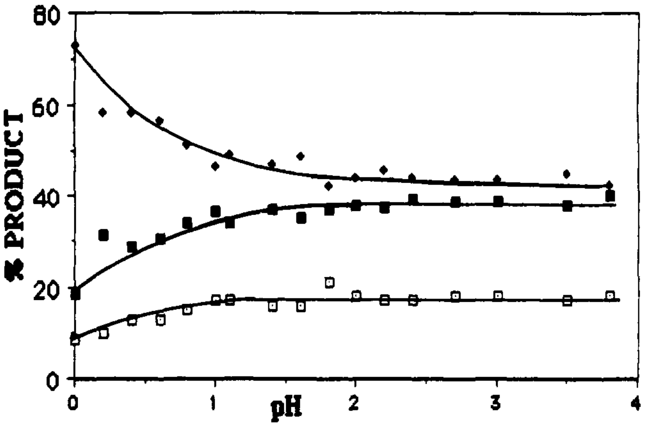


Figure 5. Olefin distribution of the products of the β-elimination reactions as a function of pH, measured in solutions containing 2 M 2-butanol, 2 × 10^{-3} M H_2O_2, and 5 × 10^{-3} M Cr^{2+}(aq), saturated with helium: (◆) (upper curve) % *cis*-2-butene; (■) (middle curve) % 1-butene; (▣) (lower curve) % *trans*-2-butene.

Table II. Specific Rates of β-Elimination Reactions of $(H_2O)_5Cr^{III}$–R Complexes[a]

–R	k_0, s^{-1}	k_{H^+}, M^{-1} s^{-1}
$-CH_2CH_2OH$	2.0	1.4 × 10^4
$-CH_2CH_2OCH_2CH_3$[b]	<0.1	4.6 × 10^3
$-CH(CH_3)CH_2OH$	2.1 × 10	1.1 × 10^5
$-CH(CH_3)CH(CH_3)OH$	2.5 × 10^2	9.8 × 10^4
$-CH_2C(CH_3)_2OH$[c]	1.0 × 10^2	2.7 × 10^6[d]
$-CH(OH)CH_2OH$[c]	>5 × 10^5 s^{-1}	
$-CHOCH_2CH_2OCH_2$[c]	<2 × 10^{-2}	4.8 × 10^{-1}

[a] Acid-independent path, k_0, acid-dependent path, k_{H^+}. [b] Reference 22. [c] Reference 7b. [d] Goldstein et al. To be published. This result corrects the value in ref 7b, which was probably a printing error.

Substituent Effects on the Rates of β-Hydroxyl Elimination Reactions. The observed rates of the β-elimination reactions (18)

$$(H_2O)_5Cr^{III}—CH(R^1)C(R^2)(R^3)OH^{2+} \rightarrow Cr(H_2O)_6^{3+} + CHR^1{=}CR^2R^3 \text{ or } (H_2O)_5Cr\{CHR^1{=}CR^2R^3\}^{3+} + OH^- \quad (18)$$

are independent of [alkene], [Cr^{2+}], [N_2O], pulse intensity and wavelength but are linearly dependent on [H_3O^+] where $k_{ob} = k_0 + k_{H^+}[H_3O^+]$. In Table II are summarized the rates of all the β-elimination reactions of $(H_2O)_5Cr^{III}–CH(R^1)C(R^2)(R^3)OR^{2+}$ complexes reported till now.

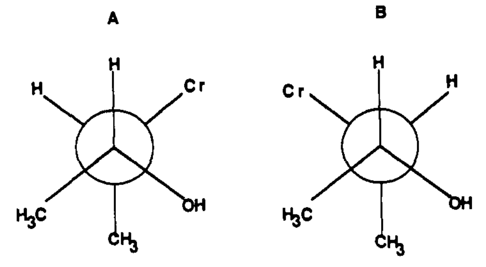
It is of interest to note that in only two of the systems studied so far, the complexes $(H_2O)_5Cr–CH_2C(CH_3)_2OH^{2+}$ and $(H_2O)_5Cr^{III}–CH(CH_3)CH(CH_3)OH^{2+}$, do the β-elimination reactions result in the formation of relatively stable complexes with a d→π bond between a tervalent chromium and an olefin. Probably, such complexes are also being formed in the other systems studied, but the rates of their decomposition are considerably higher than the rates of the corresponding β-elimination reactions.

The results in Table II point out that substituents have a considerable effect on the rates of β-elimination reactions. The results indicate that substitution of a hydrogen by a methyl group, which is a better electron-donating group, increases k_0 and k_{H^+} by different degrees when a methyl is substituted on the α-carbon or the β-carbon. However, as an analogous study on copper[9] and cobalt[11] complexes resulted in different orders of reactivities, it seems too early to discuss the effect of substituents on the rates of these reactions.

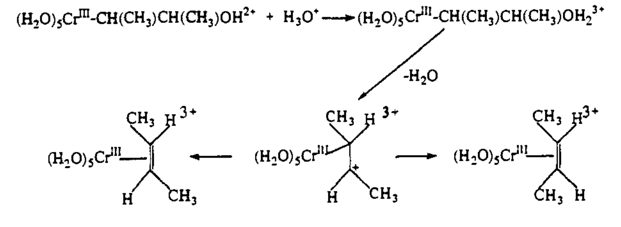
Kinetics of Decomposition of the Cr(III) d→π Complexes. The hydrolysis of the chromium d→π complexes yields tervalent chromium and the corresponding alkene (in the system $(H_2O)_5Cr\{CH(CH_3){=}CH(CH_3)\}^{3+}$ either *cis*- or *trans*-2-butene is the product—see below) via

$$(H_2O)_5Cr\{CHR^1{=}CHR^2\}^{3+} \rightarrow Cr^{3+}(aq) + CHR^1{=}CHR^2 \quad (19)$$

Chart I



Scheme I



The rates of reaction 19 is independent of [alkene], [Cr^{2+}], [N_2O], pulse intensity, and wavelength, but it is pH dependent. The rate obeys the equation $k_{ob} = k_1 + k_2[H_3O^+]$. The values for $(H_2O)_5Cr\{CH_2{=}CH(CH_3)_2\}^{3+}$ and $(H_2O)_5Cr\{CH(CH_3){=}CH(CH_3)\}^{3+}$ are k_1 = 1.4 × 10^{-4} and 0.8 s^{-1} and k_2 = 3.9 × 10^{-4} and 6.7 M^{-1} s^{-1}, respectively. Plausible mechanisms for the acid-catalyzed path are discussed below.

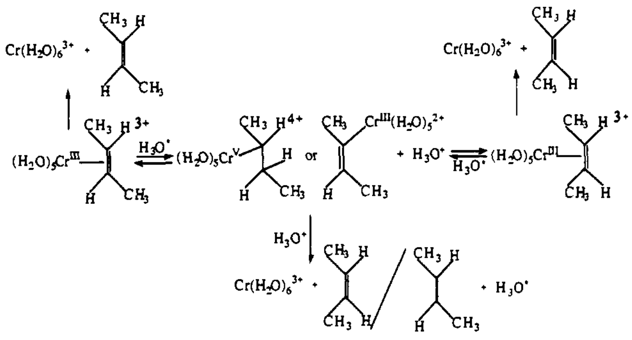
Stereoselectivity in the Production of 2-Butene from $(H_2O)_5Cr^{III}–CH(CH_3)CH(CH_3)OH^{2+}$. The data in Table I point out that the relative yields of *cis*- and *trans*-2-butene depend on the pH. As 2-butene is formed via the consecutive reactions (11), (12), and (19), the observed stereoselectivity must be due to one, or several, of these reactions. (It is reasonable to assume that the steric configuration around the carbon atom with the unpaired electron in $^{\bullet}CH(CH_3)CH(CH_3)OH$ is planar, and therefore, the stereoselectivity cannot stem from the reaction leading to its formation.)

The product of reaction 11, $(H_2O)_5Cr^{III}–CH(CH_3)CH(CH_3)OH^{2+}$, is a mixture of two diastereoisomers, as shown in Chart I.

As reaction 11 is fast, and as probably the two diastereoisomers do not differ considerably energetically, they are expected to be formed in equal yields. The β-elimination process yielding intermediate II is expected to occur by an attack of the chromium on the β-carbon via one of the two plausible directions. If the attack (which is followed by the elimination of the OH^- group, reaction 12 is from the side above the plane of the page in Chart I, then diastereoisomer A will produce *trans*-2-butene and diastereoisomer B will produce *cis*-2-butene, whereas if the attack is from under plane of the page, the reverse products are expected. It is reasonable to expect that the non-acid-catalyzed route of reaction 12 proceeds via one of these mechanisms. It is therefore not surprising that the relative yield of *cis*- and *trans*-2-butene at pH 3.8, where over 90% of the 2-butenes are formed via this route, is 1/1. This result indeed corroborates these two assumptions.

The observation that in acidic solutions the relative yield of *cis*- and *trans*-2-butene is considerably larger than 1 seemed to suggest that the stereoselectivity of the acid-catalyzed route of reaction 12 differs considerably from that of the acid-independent route. Such a stereospecificity could stem from the reaction sequence in Scheme I if the carbonium-containing intermediate prefers a collapse to the cis isomer over the trans isomer. However, a detailed analysis of the data indicates that at pH 1.7 about 90% of reaction 12 proceeds via the acid-catalyzed route whereas at this pH the relative yield of *cis*- and *trans*-2-butene is still similar to that observed at pH 3.8 (Table I). The results thus clearly indicate that the stereospecificity observed in the more acidic solutions is not due to reaction 12; i.e., the origin of the stereo-

Scheme II



specificity is not the β-elimination step in the reaction mechanism.

It is therefore to be concluded that the observed stereospecificity in acidic solutions originates from the acid-catalyzed route of reaction 19, $k_{19} = (0.8 + 6.7[H_3O^+])$ s^{-1} (Figure 2b). The change in the relative yield of the 2-butenes (Table I) indeed occurs mainly in the pH range 0–1.0, as predicted by this rate law. In the following paragraphs are discussed several mechanisms that might explain the acid-catalyzed route of reaction 19 and its contribution to the stereospecificity observed. The results require that the following two general features will be taken into account.

(1) The mechanism has to include an acid-catalyzed isomerization reaction for the Cr(III) d$\rightarrow\pi$ complex. This is required because the results above pH 3 clearly point out that no isomerization between the two Cr(III) d$\rightarrow\pi$ complexes occurs. (If such a process would occur, it is reasonable to assume that one of the two complexes will be more stable and therefore a different product ratio would be expected.)

(2) The mechanism has to include an acid-catalyzed decomposition of the Cr(III) d$\rightarrow\pi$ complex, reaction 19. It should be pointed out that both processes probably contribute to the stereospecificity observed.

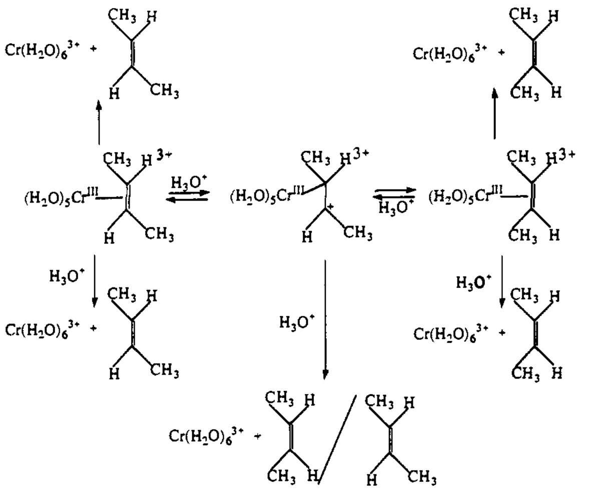
The following reaction schemes seemed to be plausible explanations of the result and are therefore discussed in detail:

(a) The first mechanism considered is that a proton adds to the olefin and is then eliminated; alternatively, one could envisage an elimination of a proton in the first step followed by a proton addition in the second step, where both steps, in both mechanisms, are acid catalyzed, as depicted in Scheme II. Both of these mechanisms are ruled out because they require that considerable labeling by deuterium be observed when the experiments are carried out in D_2O. As no labeling was observed, these reaction schemes do not fit the experimental results. These conclusions corroborate earlier observations on the decomposition of $(H_2O)_5Cr\{CH_2{=}C(CH_3)_2\}^{3+}$.[13]

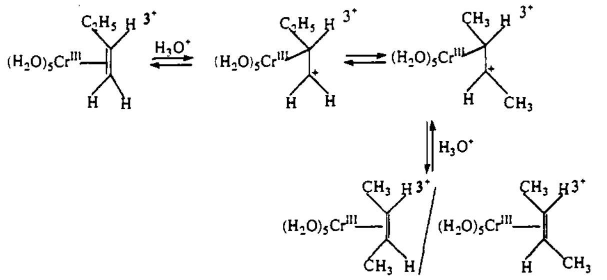
(b) Alternatively, it is plausible that the Cr(III) d$\rightarrow\pi$ complex is in equilibrium with an isomeric species in which the chromium is bound to one of the two carbon atoms by a σ bond, while the second carbon is a carbonium ion. The latter clearly provides a mechanism for isomerization. The decomposition of the complex to the final products can occur via hydrolysis of the Cr(III) d$\rightarrow\pi$ complex or via hydrolysis of the carbonium-containing intermediate, as depicted in Scheme III. Both schemes are in accord with all the experimental observations. It is not clear what the detailed role of H_3O^+ is in catalyzing the transformation from the Cr(III) d$\rightarrow\pi$ complex to its isomeric form containing the carbonium ion. It is believed that H_3O^+ catalyzes the hydrolysis step via binding to the π bond.

Thus, the results point out that the stereospecificity observed in this system does not stem from the β-elimination step but, rather surprising, from the acid-catalyzed hydrolysis of the d$\rightarrow\pi$ complex formed in this reaction. This conclusion also explains why earlier results[14] indicated that the stereospecificity of β-hydroxyl elimination reactions of this type depends on the nature of the medium in which they are performed.

Scheme III



Scheme IV



pH Dependence of the Yield of 1-Butene. The results in Table I point out that the relative yield of 1-butene and the 2-butenes is pH dependent. 1-Butene is expected to be the product of the following reaction scheme:

$$^{\bullet}CH_2CH(OH)C_2H_5 + Cr(H_2O)_6^{2+} \rightarrow (H_2O)_5Cr^{III}{-}CH_2CH(OH)C_2H_5^{2+} \quad (11a)$$

$$(H_2O)_5Cr^{III}{-}CH_2CH(OH)C_2H_5^{2+} + H_3O^+ \rightarrow (H_2O)_5Cr\{CH_2{=}CHC_2H_5\}^{3+} \quad (12a)$$

$$(H_2O)_5Cr\{CH_2{=}CHC_2H_5\}^{3+} \rightarrow Cr(H_2O)_6^{3+} + CH_2{=}CHC_2H_5 \quad (19a)$$

As the relative yield of the free radicals $^{\bullet}CH_2CH(OH)C_2H_5$ and $^{\bullet}CH(CH_3)CH(CH_3)OH$ is expected to be pH independent,[17] the observed pH dependence of the relative yield has to stem from a pH-dependent isomerization of one of the following pairs: (1) $^{\bullet}CH_2CH(OH)C_2H_5$ and $^{\bullet}CH(CH_3)CH(CH_3)OH$; (2) $(H_2O)_5Cr^{III}{-}CH_2CH(OH)C_2H_5^{2+}$ and $(H_2O)_5Cr^{III}{-}CH(CH_3)CH(CH_3)OH^{2+}$; (3) $(H_2O)_5Cr\{CH_2{=}CHC_2H_5\}^{3+}$ and $(H_2O)_5Cr\{CH(CH_3){=}CH(CH_3)\}^{3+}$.

EPR data on analogous free radicals[21] do not suggest that isomerization of the free radicals occurs. The observation that the pH dependence of the relative yield of 1-butene and the 2-butenes is similar to (Figure 6), if not identical with, the pH dependence of the relative yield of *trans*- and *cis*-2-butene suggests that both isomerization processes occur via a similar mechanism. It is therefore suggested that the isomerization process occurs via the mechanisms described in Scheme IV.

It should be pointed out that a simple calculation proves that even if all the 1-butene that isomerizes into 2-butene is transformed into *cis*-2-butene, this process cannot cause the observed changes in the *cis*- to *trans*-2-butene ratio.

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Concluding Remarks. The results obtained in this study lead to the following conclusions: (1) Complexes with chromium(III)–alkyl σ bonds that have a hydroxyl substituent on the β-carbon undergo fast, acid-catalyzed β-elimination reactions. (2) The product of the latter reaction is a d$\rightarrow\pi$ complex between chromium(III) and the olefin formed. This complex is relatively long-lived when at least two methyl substituents are bound to the olefin. (3) The rate of the β-elimination reaction is considerably affected by the number, and site of binding, of methyl substituents. (4) The stereospecificity in the decomposition of $(H_2O)_5Cr^{III}$–$CH(CH_3)CH(CH_3)OH^{2+}$ stems from the acid-catalyzed hydrolysis of the d$\rightarrow\pi$ complex, intermediate II, and not from the β-elimination reaction. (5) The formation of the d$\rightarrow\pi$ complex, intermediate II, catalyzes in acid solutions the formation of the thermodynamically less stable *cis*-2-butene vs the more stable *trans*-2-butene.

Acknowledgment. We wish to thank Professors J. H. Espenson, R. Breslow, and M. Sprecher for helpful discussions. This study was supported by the U.S.-Israel Binational Science Foundation (BSF), Jerusalem, Israel and the Israel Atomic Energy Committee. We thank the late Mr. Haim Klein and Mr. David Carmi for technical assistance. D.M. expresses his thanks to Mrs. Irene Evens for her continuous interest and support.

Geometric Conformations of Intermediates of B_{12} Catalysis by X-ray Edge Spectroscopy: Co(I) B_{12}, Co(II) B_{12}, and Base-Off Adenosylcobalamin

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Abstract: Geometric conformations for the cobalt(I) and cobalt(II) B_{12} intermediates in solution are examined by X-ray edge spectroscopy. Integration of 1s-3d and 1s-4p + SD (shakedown) transitions of edge spectra facilitates a direct comparison of relative preedge intensities of the lower valence B_{12} intermediates to model compounds of known structure. Our results indicate that the structure of the cobalt(I) and cobalt(II) forms of B_{12} in solution are distorted square-planar and distorted square-pyramidal, respectively. Base-off Co(III) adenosylcobalamin, generated by acidification, is shown to be a distorted octahedron where the axial 5,6-dimethylbenzimidazole (DMB) ligand is replaced by a water molecule at low temperature. The demonstration that Co(I) B_{12} has a detached DMB axial ligand indicates that cleavage of this bond is required for enzyme reactions like those catalyzed by methionine synthetase (Frasca et al. *Biochemistry* **1988**, *27*, 8458). Such a mechanism must be distinct from those of enzymes involved in homolytic cleavage, where EXAFS studies show a strengthening of the bond from cobalt to DMB for the Co(II) B_{12} species (Sagi et al. *J. Am. Chem. Soc.* **1990**, *112*, 8639). Shifts in the cobalt absorption threshold (main peak of the first derivative spectrum) are shown to be characteristic of the effective charge on the cobalt ion. Edge shifts to lower energy for the reduction of Co(III) to Co(II) to Co(I) cobalamins and cobaloximes follow a linear relationship between the absorption threshold position and the effective charge. The σ donor effects of alkyl ligands bonded to cobalt are also evidenced by shifts in the threshold. A reduced positive charge for these compounds may be important in lowering the barrier to formation of lower oxidation states upon cleavage of the cobalt–carbon bond.

Introduction

B_{12} coenzymes are recognized for playing a key role in a number of important biochemical reactions of metabolism and providing a model system for cis–trans effects in coordination chemistry. To better understand these enzyme reaction mechanisms it is necessary to know the structure of lower valence cobalt(I) and cobalt(II) B_{12} intermediates. Also, cleavage of the 5,6-dimethylbenzimidazole (DMB) base trans to the Co–C bond in alkylcobalamins, and its possible replacement by protein ligands, has been proposed as a possible mechanism for influencing cobalamin reactivity. However, this structure has not been fully characterized.

X-ray crystallographic studies have reported accurate structures for dicyanocobinamide,[1] adenosylcobalamin,[2] and methylcobalamin.[3] Dicyanocobinamide is a B_{12} analogue that contains cyanide groups in the fifth and sixth (axial) positions. Adenosyl- and methylcobalamin both contain a DMB base in the fifth axial position and 5′-deoxyadenosyl and methyl groups in the sixth position. Recently, the structure of cobalt(II) B_{12} was reported by both X-ray crystallography[4] and extended X-ray absorption fine structure (EXAFS) spectroscopy.[5] However, the structures of a number of metabolically and enzymatically important forms, including cyanocobalamin,[6,7] have not been solved satisfactorily due to difficulty in obtaining high quality crystals. Also, some concerns about possible differences in structure for crystal and solution conditions have been raised for cobalamins.[4,5,8] The advantage of X-ray absorption spectroscopy is that it provides direct structural information in solution.

Analysis of 1s-3d and 1s-4p + SD transitions as well as the cobalt absorption edge provides detailed information about the central metal of coordination compounds. Our results indicate

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