

KINETIC STABILITY OF σ -BONDED $[(\text{H}_2\text{O})_5\text{CrCH}_2\text{COOH}]^{2+}$ ION

P. ŠEVČÍK and D. JAKUBCOVÁ

*Department of Physical Chemistry,
Comenius University, 816 31 Bratislava*

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Kinetic stability of $[(\text{H}_2\text{O})_5\text{CrCH}_2\text{COOH}]^{2+}$ ion containing bond between chromium and carbon has been studied in an aqueous solution of perchloric acid. The reaction of the above ion with Br_2 has been also investigated. Kinetic parameters for the aquation of $[(\text{H}_2\text{O})_5\text{CrCH}_2\text{COOH}]^{2+}$ ion are as follows: the pseudo-first order rate constant $k_{\text{obs}} = 1.66 \cdot 10^{-4} \text{ s}^{-1}$ at 323 K (independent of $[\text{H}^+]$), $\Delta H^\ddagger = 96.1 \text{ kJ mol}^{-1}$, and $\Delta S^\ddagger = -23.7 \text{ J mol}^{-1} \text{ K}^{-1}$. The aquation is catalysed by $\text{Cr}_{\text{aq}}^{2+}$ ions. A direct redox reaction of the organochromium(III) ion with selected oxidizing agents (O_2 , H_2O_2 and Cu^{2+}) has not been observed. The chromium-carbon σ bond in $[(\text{H}_2\text{O})_5\text{CrCH}_2\text{COOH}]^{2+}$ ion is readily cleaved by electrophilic substitution reaction with Br_2 .

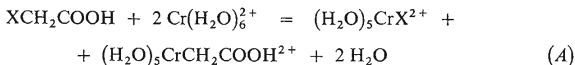
Cohen and Meyerstein¹ have measured the rates of reactions of several aliphatic radicals with Cr^{2+} ions in aqueous solutions of perchloric acid. The rate constant $k = 2.5 \cdot 10^8 \text{ l mol}^{-1} \text{ s}^{-1}$ for the reaction of CH_2COOH radical with $\text{Cr}_{\text{aq}}^{2+}$ taking place under formation of Cr—C σ bond was determined¹ by pulse radiolysis. The high value of the rate constant of this reaction is also predicted based on the reaction mechanism of oxidation of $\text{Cr}_{\text{aq}}^{2+}$ ions by monohalogenoacetic acids². This mechanism involves inner-sphere halogen transfer followed by a fast reaction of the CH_2COOH radical formed with another $\text{Cr}_{\text{aq}}^{2+}$ ion with formation of an organochromium(III) complex. The reaction of XCH_2COOH ($\text{X} = \text{Cl}, \text{Br}, \text{and I}$) with $\text{Cr}_{\text{aq}}^{2+}$ ion renders it possible to prepare the above $[(\text{H}_2\text{O})_5\text{CrCH}_2\text{COOH}]^{2+}$ complex.

For the mechanism of the cleavage of the σ bond between carbon and chromium no systematic and extensive data are at present available. The greatest attention has so far been paid to hydrolysis of alkyl(ene)chromium(III) complexes³, aquation of $(\text{H}_2\text{O})_5\text{CrL}^{2+}$ (L are small acyclic anion)⁴ and to aquation of $[(\text{H}_2\text{O})_5\text{CrCF}_3]^{2+}$ the only fluoroorganochromium(III) complex prepared so far⁵. Recently, Espenson and Williams have reported⁶ on the results of a kinetic study of bromination of $[(\text{H}_2\text{O})_5\text{CrR}]^{2+}$ (R = simple alkyls, halogenoalkyls and 4-pyridinomethyl). In the case of benzylchromium(III) ion, the first example of isolated organochromium(III) complex⁷, the Cr—C σ bond has been found to undergo oxidative cleavage⁸.

In this work we have studied the kinetic stability of σ -bonded $[(\text{H}_2\text{O})_5\text{CrCH}_2\text{COOH}]^{2+}$ ion. The main attention has been paid to the kinetics of aquation in aqueous perchloric acid solution, decomposition of this ion in the presence of oxidizing agents (O_2 , H_2O_2 , and Cu^{2+}), and to the reaction of the above ion with bromine.

EXPERIMENTAL

Chemicals. The $[(\text{H}_2\text{O})_5\text{CrCH}_2\text{COOH}]^{2+}$ complex has been prepared by the redox reaction (A) where X is bromine (in most cases) or iodine.



Monochloroacetic acid is not suitable, since its redox reaction with Cr^{2+} proceeds at a relatively slow rate. A total of 10 ml of the reaction solution containing 0.4M- XCH_2COOH and approximately 0.2M- Cr^{2+} in 0.5M- HClO_4 was allowed to react for 6–7 half times (c. 1 minute for X = I and 10 minutes for X = Br) in an atmosphere of nitrogen. The reaction mixture was then diluted with cold distilled water so that ionic strength has been lowered below 0.1 mol/l. The Cr(III) complexes formed were isolated by column chromatography with the use of Dowex 50 W-X2 (8 × 1 cm column) which was in the H^+ form.

Both 2+ charged complexes so formed were eluted with 0.5M- HClO_4 . The green fraction of the $(\text{H}_2\text{O})\text{CrX}^{2+}$ complex was eluted first, followed by the red organochromium(III) complex. On using ICH_2COOH the $[(\text{H}_2\text{O})\text{CrI}]^{2+}$ complex formed was partially aquated to give $\text{Cr}(\text{H}_2\text{O})_6^{3+}$. The best fractions of the red band have been collected. Absorption spectra of these fractions which were formed by $\text{Cr}_{\text{aq}}^{2+} + \text{XCH}_2\text{COOH}$ reactions (X = Br and I) are shown in Fig. 1. A value of ϵ_{273} found by us ($3.9 \cdot 10^3 \text{ l mol}^{-1} \text{ cm}^{-1}$) compares better with analogous spectra than a value of $9.6 \cdot 10^2$ reported earlier¹. The other chemicals used were analytically pure. The preparation of a solution of $\text{Cr}_{\text{aq}}^{2+}$ ions was reported elsewhere⁹.

Analyses. Gas chromatography was used to identify organic products of the aquation of $[(\text{H}_2\text{O})_5\text{CrCH}_2\text{COOH}]^{2+}$. Analyses were carried out on Fractovap 2407 apparatus (Carlo Erba) equipped with a flame-ionisation detector. The carrier gas was nitrogen. The 0.4×200 cm column was filled with 10% dodecyl phthalate and 1% H_3PO_4 on Chromosorb W (60–80 mesh). The column temperature was 358 K. In a typical example, 4M-NaOH was added to the reaction mixture after aquation till the mixture became alkaline. The mixture was evaporated to dryness *in vacuo*, then 10 ml of diethyl ether were added and the mixture was acidified by adding dropwise concentrated sulphuric acid. The mixture was filtered through CaCl_2 column (5 × 0.5 cm).

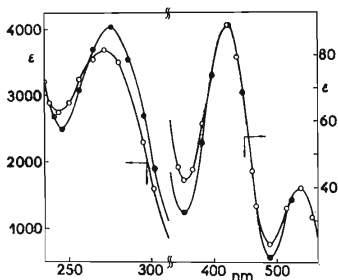


FIG. 1

Absorption Spectra of the Red Product of $\text{Cr}_{\text{aq}}^{2+} + \text{XCH}_2\text{COOH}$ Reactions

X = I (○), Br (●).

The ether extract was fed to the apparatus in 0.5 μl amounts. The solution of acetic acid treated analogously to the above samples was used as the standard.

Cr(III) products of various reactions of $[(\text{H}_2\text{O})_5\text{CrCH}_2\text{COOH}]^{2+}$ ion were separated from the other products by chromatography with the use of an ion exchanger. The column was packed with Dowex 50WX2 which was in the H^+ form. The reaction with Br_2 was performed with bromine in excess. The unreacted bromine was removed from the reaction mixture by a stream of nitrogen. Prior to introduction of Cr(III) complexes on the ion exchanger column, the ionic strength was adjusted to below 0.1 mol/l by diluting the mixture with distilled water. To remove Cr(III) products of the aqutation and bromination of the organochromium(III) ion, it was necessary to use 1M- HClO_4 . Cr(III) products were identified by comparing their absorption spectra with those reported. The total content of chromium in fractions was determined spectrophotometrically, after oxidation to the chromate by alkaline H_2O_2 solution. The absorbance at 372 nm was measured (CrO_4^{2-} , $\epsilon_{372} = 4815 \text{ l mol}^{-1} \text{ cm}^{-1}$). Spectrophotometric measurements were made on Specord UV VIS (Zeiss, Jena) or MOM 204 (Hungary) instrument, using 1–5 cm air-proof quartz cells.

Free Br^- ions present in the reaction mixture after the reaction of the organochromium(III) ion with bromine were determined by potentiometric titration. After removal of the excess bromine by nitrogen stream, 0.01M- AgNO_3 solution was added. The silver electrode was used as the indicator electrode and the standard calomel electrode as the reference. The pH-meter used was of OP 204/1 type (Radelkis, Hungary).

Stoichiometric and rate measurements. Stoichiometry of the reaction of $[(\text{H}_2\text{O})_5\text{CrCH}_2\text{COOH}]^{2+}$ with Br_2 was determined by spectrophotometric titrations, as described in ref.⁶. The absorbance of the reaction mixture was measured at 273 and 417 nm, i.e. at the absorption maxima of the organochromium(III) complex, in dependence upon the amount of bromine added. Bromine concentration was determined spectrophotometrically, by using a value of ϵ_{452} equaling to $103 \text{ l mol}^{-1} \text{ cm}^{-1}$ reported earlier⁶. At the wavelengths chosen, bromine has $\epsilon_{273} = 192 \text{ l mol}^{-1} \text{ cm}^{-1}$ (the value significantly lower compared to $\epsilon_{273} = 3786 \text{ l mol}^{-1} \text{ cm}^{-1}$ for $[(\text{H}_2\text{O})_5\text{CrCH}_2\text{COOH}]^{2+}$) and $\epsilon_{417} = 96 \text{ l mol}^{-1} \text{ cm}^{-1}$ (comparable to $\epsilon_{417} = 89.5 \text{ l mol}^{-1} \text{ cm}^{-1}$ for the organochromium(III) complex).

Kinetics of the reactions of the organochromium(III) ion were followed by measuring a decrease in absorbance at 273 and 417 nm (bromination in only UV region). Fractions taken from the thermostated reaction flask were introduced into cells. The reaction with bromine was followed directly in the cell at the constant temperature of 293 K. Purified nitrogen was used as an inert atmosphere in the study of kinetics of aqutation and in some comparative measurements. A decrease in the concentration of $[(\text{H}_2\text{O})_5\text{CrCH}_2\text{COOH}]^{2+}$ ion with time could be described as a rule by first-order equation and the rate constants were determined from the negative slope of the $\ln(A_t - A_\infty) = f(t)$ dependence. For some reactions of $[(\text{H}_2\text{O})_5\text{CrCH}_2\text{COOH}]^{2+}$ with bromine, equimolar concentrations of the reactants were used and the second-order rate constants were calculated from the linear $1/(A_t - A_\infty) = f(t)$ dependence.

RESULTS

Aqutation of $[(\text{H}_2\text{O})_5\text{CrCH}_2\text{COOH}]^{2+}$ ion. The products of aqutation of the organochromium(III) ion in aqueous perchloric acid solutions were identified as $\text{Cr}(\text{H}_2\text{O})_6^{3+}$ ions and acetic acid. Experiments aimed at increasing the yield of acetic acid (56.8%) have not been performed. The nature of the products is not influenced

by air oxygen. The reaction observed is obviously the following (equation (B)).



By kinetic study of the aquation it was found that the pseudofirst order rate constant (defined by Eq. (1)), $k_{\text{obs}} = 1.66 \cdot 10^{-4} \text{ s}^{-1}$ for 323 K and an ionic strength of 1 mol/l, does not depend upon hydrogen ion concentration within the 0.05–1M- HClO_4 region.

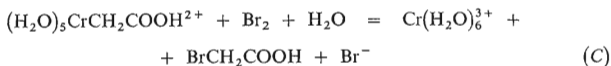
$$-\frac{d[(\text{H}_2\text{O})_5\text{CrCH}_2\text{COOH}^{2+}]}{dt} = k_{\text{obs}} \cdot [(\text{H}_2\text{O})_5\text{CrCH}_2\text{COOH}^{2+}] \quad (1)$$

The ionic strength was adjusted by NaClO_4 . The activation parameters obtained from the temperature dependence of the aquation rate constant in 0.5M- HClO_4 according to the Eyring equation had the following values: $\Delta H^\ddagger = 96.1 \pm 2.8 \text{ kJ} \cdot \text{mol}^{-1}$ and $\Delta S^\ddagger = -23.7 \pm 9 \text{ J mol}^{-1} \text{ K}^{-1}$.

The rate of decomposition of the $[(\text{H}_2\text{O})_5\text{CrCH}_2\text{COOH}]^{2+}$ ion in an aqueous solution of perchloric acid increases with $\text{Cr}_{\text{aq}}^{2+}$ concentration. k_{obs} in the presence of 0.02, 0.1, and 0.2M- $\text{Cr}_{\text{aq}}^{2+}$ ions is $1.25 \cdot 10^{-4}$, $8.36 \cdot 10^{-4}$, and $1.23 \cdot 10^{-3} \text{ s}^{-1}$ at 293 K, 0.5M- HClO_4 and an ionic strength of 0.5 mol/l. From the linear dependence of k_{obs} upon Cr^{2+} concentration the catalytic rate constant $k_{\text{Cr}_{\text{aq}}^{2+}} = 6.8 \cdot 10^{-3} \text{ l} \cdot \text{mol}^{-1} \text{ s}^{-1}$ at 293 K, has been determined for 0.5M- HClO_4 .

Decomposition of $[(\text{H}_2\text{O})_5\text{CrCH}_2\text{COOH}]^{2+}$ ion in the presence of O_2 , H_2O_2 , and Cu^{2+} ions. The rate of decomposition of the organochromium(III) ion was investigated in 0.5M- HClO_4 in the presence of saturated oxygen solution ($\approx 10^{-3}\text{M-O}_2$) at 323 K, in the presence of $5 \cdot 10^{-3}\text{M}$ and $5 \cdot 10^{-2}\text{M-H}_2\text{O}_2$ at 313 and 323 K, and in the presence of $5 \cdot 10^{-3}\text{M-Cu}^{2+}$ at 313, 323, and 333 K. In all cases the oxidizing agent was used in sufficient excess. The pseudo-first order constant $k_{\text{obs}} = 1.62 \pm 0.09 \cdot 10^{-4} \text{ s}^{-1}$ (at 323 K) was identical for all the oxidizing agents. With regard to the different values of the activation enthalpies of eventual redox reaction and aquation, k_{obs} was measured at varying temperatures. The activation parameters determined did not differ from the values obtained for the aquation of the $[(\text{H}_2\text{O})_5\text{CrCH}_2\text{COOH}]^{2+}$ ion in the absence of oxidizing agents.

Reaction of $[(\text{H}_2\text{O})_5\text{CrCH}_2\text{COOH}]^{2+}$ with bromine. Bromination of the organochromium(III) complex proceeds according to equation (C), which is demonstrated by the following results. Stoichiometry of the reaction was determined by spectrophotometric titrations. The ratio of the reactants consumed



$\Delta[\text{Br}_2]/\Delta[(\text{H}_2\text{O})_5\text{CrCH}_2\text{COOH}^{2+}]$, which was determined at 273 and 414 nm, equals to one. The analysis of Cr(III) product by ion-exchanger chromatography (after removal of the excess bromine) showed that $\text{Cr}(\text{H}_2\text{O})_6^{3+}$ ion (not the green $(\text{H}_2\text{O})_5\text{CrBr}^{2+}$ complex) is formed exclusively. Potentiometric titrations revealed that 0.87 mol of free Br^- ions are produced per 1 mol of the reacted $[(\text{H}_2\text{O})_5\text{CrCH}_2\text{COOH}]^{2+}$. The above results were taken as indicative of also quantitative stoichiometry of the formation of monobromoacetic acid.

Kinetics of the reaction of $[(\text{H}_2\text{O})_5\text{CrCH}_2\text{COOH}]^{2+}$ with Br_2 was examined in 0.5M- HClO_4 at 293 K, ionic strength being 0.5 mol/l. At equivalent concentrations the changes in concentrations of the reactants obeyed second-order kinetic equation. Reaction rate increased with bromine concentration. In excess bromine, the pseudo-first order rate constant determined and divided by bromine concentration was identical with the value of the second-order rate constant. The rate law can be thus expressed by Eq. (2) where $k = 1.15 \pm 0.18 \cdot 10^3 \text{ l mol}^{-1} \text{ s}^{-1}$ for 0.5M- HClO_4 and 293 K.

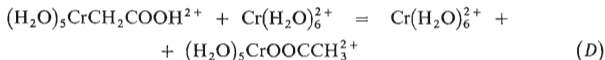
$$-\frac{d[(\text{H}_2\text{O})_5\text{CrCH}_2\text{COOH}^{2+}]}{dt} = k[(\text{H}_2\text{O})_5\text{CrCH}_2\text{COOH}^{2+}] \cdot [\text{Br}_2] \quad (2)$$

DISCUSSION

It is of interest that a good electrophilic agent such as H_3O^+ which is present in high concentration in aqueous solutions of perchloric acid does not react directly with the $[(\text{H}_2\text{O})_5\text{CrCH}_2\text{COOH}]^{2+}$ ion. Aquation rate of this ion does not depend upon concentration of hydroxonium ions. This fact does not exclude, however, that the solvent molecule (H_2O) enters the activated complex. A value of ΔH^\ddagger (96.1 kJ mol^{-1}) indicates the cleavage of a relatively strong bond and the negative $\Delta S^\ddagger = -23.7 \text{ J} \cdot \text{mol}^{-1} \text{ K}^{-1}$ is a reasonable value for the activated complex containing solvent molecule⁵. Cr(III) products of the aquation do not exclude also that monomolecular cleavage of the Cr—C σ bond is taking place under formation of $\text{Cr}(\text{H}_2\text{O})_6^{3+}$ and HOOCCH_2^- . However, in the acidic medium utilized it does not seem likely that this aquation leads to formation of the carbanion (which would later protonate). More probably, the proton must be available in the activated complex prior to the dissociation of the latter to products. In the case of a reaction path that is independent of perchloric acid concentration, as observed in the aquation of the $[(\text{H}_2\text{O})_5\text{CrCH}_2\text{COOH}]^{2+}$ ion, decomposition of the activated complex containing H_2O molecule could result in formation of acetic acid and $(\text{H}_2\text{O})_5\text{CrOH}^{2+}$ ion. The protonation of the latter would lead to the hexaaquochromium(III) ion observed.

Catalytic effect of $\text{Cr}_{\text{aq}}^{2+}$ ions upon the rate of aquation of $[(\text{H}_2\text{O})_5\text{CrCH}_2\text{COOH}]^{2+}$ consists likely of bridge redox reaction of Cr^{2+} with the organochromium(III) ion

according to equation (D), as indicated for analogous $[(\text{H}_2\text{O})_5\text{CrCl}_2\text{COOH}]^{2+}$ (ref.⁹)



and $[(\text{H}_2\text{O})_5\text{CrCHClCOOH}]^{2+}$ (ref.¹⁰) ions. The fact that $\text{Cr}(\text{ClO}_4)_2$ retards decomposition of the benzylchromium(III) ion⁸ in aqueous HClO_4 solution has been used to support the assumption about monomolecular homolysis of the benzylchromium(III) ion as the rate determining step. The intermediate products formed by this homolysis, Cr^{2+} and benzyl radical, undergo fast oxidation reactions by the action of oxidizing agents⁸. Our experiments have shown that the aquation of $[(\text{H}_2\text{O})_5\text{CrCH}_2\text{COOH}]^{2+}$ in the presence of oxidizing agents such as O_2 , H_2O_2 , and Cu^{2+} proceeds at the same rate in 0.5M- HClO_4 and at various temperatures as does the reaction in their absence. Hence, the direct oxidation reaction between the organochromium(III) ion and the above oxidizing agent does not take place.

On the other hand, the relatively fast bimolecular reaction of the excellent electrophilic agent, bromine, with $[(\text{H}_2\text{O})_5\text{CrCH}_2\text{COOH}]^{2+}$ indicates the possibility of the facile cleavage of the σ bond between chromium and carbon. This bromination is first order reaction in both Br_2 and $[(\text{H}_2\text{O})_5\text{CrCH}_2\text{COOH}]^{2+}$. We can thus exclude the mechanism which involves homolysis of $\text{Cr}-\text{C}$ bond as the rate determining step, *i.e.* $\text{CrL}^{2+} \rightarrow \text{Cr}^{2+} + \text{L}$. The reaction proceeds as bimolecular $\text{S}_{\text{E}}2$ substitution on the carbon with the so-called open configuration of the activated complex, since experiments on ion exchangers proved that the bromination product are separated $\text{Cr}(\text{H}_2\text{O})_6^{3+}$ and Br^- ions. Therefore, bimolecular mechanism in which the



activated complex contains a four-atomic closed structure, *i.e.* $\text{Cr}-\text{C}$, can be excluded.

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