

Trichloromethylpentaquo chromium(III) Ion

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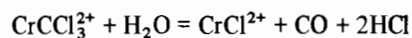
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Dodd and Johnson [1] prepared the mono- and dihalogenomethylchromium(III) ions containing a metal-carbon σ bond in the homogeneous reactions of Cr^{2+} with methylene dihalides and by the analogous reaction of Cr^{2+} with halogeno-forms. The reduction of carbon tetrachloride with chromous perchlorate gave an unstable red solution, believed to contain the trichloromethylchromium(III) ion, which rapidly decomposed [1].

Ion exchange chromatography enabled us to separate the trichloromethylchromium(III) from the other products formed by the reaction between Cr^{2+} and CCl_4 by the following procedure. The solution of $\text{Cr}(\text{ClO}_4)_2$ was added under nitrogen to an ice-cooled stirred solution containing CCl_4 in $\text{H}_2\text{O}-\text{CH}_3\text{OH}-\text{HClO}_4$. A solution of $(0.4-1) \times 10^{-1} M \text{Cr}^{2+}$ and $5 \times 10^{-2} M \text{CCl}_4$ in $0.1-0.5 M \text{HClO}_4$ and 50% (v) methanol was allowed to react under N_2 essentially to completion (2 min). The colour change from sky blue Cr^{2+} to red follows without delay. The product solution (2 ml) was diluted by ice-cooled distilled water to an ionic strength of less than $0.1 M$. This solution was quantitatively transferred to a $6 \times 1 \text{ cm}$ ice-cooled Dowex 50W-X2 (200-400 mesh) cation-exchange column in H^+ form. The sample was eluted with $0.5 M$ or $1 M \text{HClO}_4$. The first fraction eluted was green CrCl^{2+} ion. The second fraction of the chromium bands could be obtained free of CrCl^{2+} for the determination of product spectra. The fractions collected were analyzed for total chromium (after oxidation of the sample by H_2O_2 in base, CrO_4^{2-} , $\epsilon_{372} = 4.82 \times 10^3 \text{ l mol}^{-1} \text{ cm}^{-1}$). Under optimum conditions, the amounts of chromium present in the green and red fractions were equal and accounted for all the Cr^{2+} used in the reduction.

The absorption spectrum of the CrCCl_3^{2+} was measured at $\sim 1^\circ \text{C}$ with a Unicam SP 1800 spectrophotometer in the visible and near-UV region. The spectrum has absorption maxima at 272 nm (ϵ 3700), 400 nm (ϵ 131) and 529 nm (ϵ 56.5) in $1 M \text{HClO}_4$. The spectrum is similar to those of the chloro-substituted complexes reported by Dodd [1] and Espenson [2].

An analysis of the chromium products of the aqutation of CrCCl_3^{2+} in $1 M \text{HClO}_4$ (spectrophotometrically after ion exchange chromatography) showed the primary reaction product to be CrCl^{2+} . The evolved gas was identified as carbon monoxide by a GC MS Varian System MAT 111 on Porapak Q (80-100 mesh) column heated to 60°C using helium as the carrier gas. Chloride content was measured by titration with standard AgNO_3 solutions potentiometrically. Chloroform and methane were not found as products of the aqutation. The stoichiometry in $1 M \text{HClO}_4$ can be represented by the equation



The kinetics of aqutation of CrCCl_3^{2+} in $1 M \text{HClO}_4$ under N_2 were followed by measuring the decrease in absorbance at 400 nm on a Unicam SP 1800 spectrophotometer. The rate constants, k_{obsd} , were evaluated from linear pseudo-first-order rate plots ($k_{\text{obsd}}^{274} = 8.6 \times 10^{-4} \text{ s}^{-1}$, $\Delta H^\ddagger \cong 91.1 \text{ kJ mol}^{-1}$ and $\Delta S^\ddagger \cong 31 \text{ J mol}^{-1} \text{ K}^{-1}$ in $1 M \text{HClO}_4$). The presence of oxygen or added Cr^{2+} did not appreciably affect the rate of aqutation. The CrCCl_3^{2+} ion is relatively labile to aqutation in aqueous acid solutions compared to the trihalo analog CrCF_3^{2+} (acid dependent rate constant $k^{298} = 8.6 \times 10^{-8} M^{-1} \text{ s}^{-1}$ [3]). The same parameter for CrCH_3^{2+} is $5.2 \times 10^{-3} M^{-1} \text{ s}^{-1}$ [4, 5].

The formation of CO in the aqutation of CrCCl_3^{2+} suggests dichlorocarbene as an intermediate. The difference in the rate of aqutation of trichloro vs trifluoro species (ca. five orders of magnitude) is consistent with the breaking of the relatively weaker carbon-chlorine bond. A plausible mechanism would be the transfer of a chlorine from carbon to the chromium accompanied by dissociation of the Cr-C bond. In this case CrCl^{2+} would be the main chromium product.

References

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