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Trichloromethylpentaaquochromium(III) Ion

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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 $Cr(ClO_4)_2$ was added under nitrogen to an ice-cooled stirred solution containing CCl_4 in H_2O–CH_3OH–$HClO_4$. A solution of $(0.4–1) \times 10^{-1}$ *M* Cr^{2+} and 5×10^{-2} *M* CCl_4 in 0.1–0.5 *M* $HClO_4$ 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 × 1 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* $HClO_4$. 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-}, $\epsilon_{372} = 4.82 \times 10^3$ l mol^{-1} 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 ~ 1 °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* $HClO_4$. 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 aquation of $CrCCl_3^{2+}$ in 1 *M* $HClO_4$ (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 aquation. The stoichiometry in 1 *M* $HClO_4$ can be represented by the equation

$$CrCCl_3^{2+} + H_2O = CrCl^{2+} + CO + 2HCl$$

The kinetics of aquation of $CrCCl_3^{2+}$ in 1 *M* $HClO_4$ 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 ($k^{274}_{obsd} = 8.6 \times 10^{-4}$ s^{-1}, $\Delta H^{\neq} \cong 91.1$ kJ mol^{-1} and $\Delta S^{\neq} \cong 31$ J mol^{-1} K^{-1} in 1 *M* $HClO_4$). The presence of oxygen or added Cr^{2+} did not appreciably affect the rate of aquation. The $CrCCl_3^{2+}$ ion is relatively labile to aquation 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} s^{-1} [3]). The same parameter for $CrCH_3^{2+}$ is 5.2×10^{-3} M^{-1} s^{-1} [4, 5].

The formation of CO in the aquation of $CrCCl_3^{2+}$ suggests dichlorocarbene as an intermediate. The difference in the rate of aquation 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

1 D. Dodd and M. D. Johnson, *J. Chem. Soc. A,* 34 (1968).
2 J. H. Espenson and J. P. Leslie, *Inorg. Chem., 15,* 1886 (1976).
3 S. K. Malik, W. Schmidt and L. O. Spreer, *Inorg. Chem., 13,* 2986 (1974).
4 W. Schmidt, J. H. Swinehart and H. Taube, *J. Am. Chem. Soc., 93,* 1117 (1971).
5 M. Ardon, K. Woolmington and A. Pernick, *Inorg. Chem., 10,* 2812 (1971).