KINETICS AND MECHANISM OF OXIDATION OF Cr(II) IONS BY TETRACHLOROMETHANE*

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Kinetics of the redox reaction of Cr(II) ions with tetrachloromethane has been studied in H_2O-CH_3OH-$HClO_4$ and H_2O-CH_3COOH-$HClO_4$. In the redox reaction 2 moles of Cr(II) are consumed per one mol of CCl_4, and $CrCl^{2+}$ and $CrCCl_3^{2+}$ ions are formed in the same amounts. Second order rate constants ($k^{293} = 2{\cdot}3\ l\ mol^{-1}\ s^{-1}$ in 50% CH_3OH, $k^{293} = 1{\cdot}66\ l\ .\ mol^{-1}\ s^{-1}$ in 50% CH_3COOH) are independent of H^+ ions concentration. The rate determining step is an inner sphere transfer of the halogen from CCl_4 to Cr(II), the Cr—Cl—C bridge structure being retained in both media.

Anet[1] observed a fast colour change of the blue solution of Cr^{2+} ions after addition of CCl_4 to green *via* red in an aqueous $HClO_4$ solution. Castro and Kray[2] studied the redox reaction of $CrSO_4$ with CCl_4 in aqueous dimethylformamide. Although their study was not kinetic, the authors noticed that the reduction of CCl_4 by $Cr(ClO_4)_2$ proceeded at a slower rate and the products were CH_4 (25%) and CO (75%). The rate of methane formation was, however, substantially slower compared to the Cr(II) ion consumption (the expected stoichiometric ratio 1 : 8 was obtained only at the end of the reaction). Dodd and Johnson[3] suppose that the red solution, which is formed in the reduction of CCl_4 by $Cr(ClO_4)_2$ in water-acetone medium contains trichloromethylchromium(III) ion which decomposes in the presence of excess Cr(II) ions or of O_2 without forming an organochromium(III) compound. Some properties of trichloromethylchromium(III) ion have been recently reported[4]. Tereda and Kiba[5] analysed gas chromatographically the products of the reaction of Cr(II) ions with CCl_4 in an aqueous HCl solution and detected tetrachloroethylene and CO but did not find CH_4, not even in traces. During the reaction, 4 mol of Cr(II) ions were consumed per 1 mol of CCl_4.

The above mentioned facts illustrate the important role of the reaction medium in the redox reaction of Cr(II) ions with CCl_4. For that reason, we decided to perform a kinetic study of this redox reaction in two media, water–methanol–perchloric acid and water–acetic acid–perchloric acid.

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EXPERIMENTAL

Materials. All stoichiometric and rate measurements were carried out under nitrogen. Nitrogen for lamps was purified by passing through a washing bottle containing Cr(II) ions which were prepared by the reaction of $KCr(SO_4)_2$ with zinc amalgam in H_2SO_4. Solutions were obtained from common chemicals of analytical grade purity and redistilled water. Reaction solutions of $Cr(ClO_4)_2$ were prepared by dissolving excess metallic chromium (99·997%, Fluka A. G., Buchs) in perchloric acid (usually 0·1M) and were storred under nitrogen. The amount of Cr(III) impurities in these solutions was determined polarographically from the ratio of the anodic limiting current of Cr(II) ions ($E_{1/2} = -0{\cdot}36$ V *vs* N.C.E. in 1M-$HClO_4$) to the height of the cathodic wave of Cr(III) ions ($E_{1/2} = -0{\cdot}98$ V *vs* N.C.E. in 1M-$HClO_4$). The content of Cr(III) impurities was 5–8% of the Cr(II) ions concentration. Total chromium concentration was determined spectrophotometrically at 372 nm with $\varepsilon = 4820$ l mol^{-1} cm^{-1} (ref.[6]), after oxidation to chromate with an alkaline H_2O_2 solution.

Analyses. Cr(III) complexes were separated from other reaction products by ion exchange chromatography. We used an all-glass column (6–15 × 1 cm) cooled by ice and packed with Dowex 50 W-X2 (200–400 mesh) in the H^+ form. Prior to introducing into the column, the ionic strength of products solution was adjusted by distilled water to less than 0·1M. The $^{2+}$ charged Cr(III) complexes were eluted by 0·5M or 1 M-$HClO_4$. The product of the oxidation of Cr(II) by air oxygen, $Cr_2(OH)_2^{4+}$, was separated by 5M-$HClO_4$. The elution time and isolation of single fractions varied from several minutes to 1 hour. Single fractions of Cr(III) complexes were completely separated. Identification of the fractions and further measurements were carried out on Unicam SP 1800 and Specord UV-VIS spectrophotometers.

Stoichiometry. With regard to reported controversional data[2,5], a great attention has been paid by us to the stoichiometry of the reaction of Cr(II) with CCl_4. In polarometric titration we made use of the polarographic activity of Cr(II) ions and of the sufficient reaction rate. We titrated both $4{\cdot}9 \,.\, 10^{-2}$M-Cr(II) solution by 0·5M-CCl_4 in 40% methanol containing 1M-$HClO_4$ and $5 \,.\, 10^{-2}$M-CCl_4 by 0·45M-Cr(II) solution under the same conditions. After adding the titrating agents, the reaction was complete in 1–3 min and the value of limiting diffusion current at 0 V *vs* N.C.E. (which was read) did not change with time. It was found that in the redox reaction 2 mol of Cr(II) are consumed per 1 mol of CCl_4. This result did not vary with varying reactants concentration or with changing the co-solvent to acetic acid (Fig. 1). In an attempt to eliminate the time factor, we allowed $(2{\cdot}4-5) \,.\, 10^{-2}$M-Cr(II) solutions to react with 0·01M-CCl_4 in 50% methanol under nitrogen for 1 h and then determined the concentration of unreacted Cr(II) ions. Also these results confirmed the above stoichiometry.

Kinetics. Kinetics of the redox reaction of Cr(II) with CCl_4 in H_2O–CH_3OH–$HClO_4$ and in H_2O–CH_3COOH–$HClO_4$ was followed polarographically, using LP7 instrument. Time dependence of the limiting diffusion current of Cr(II) ions was recorded at a constant potential of $-0{\cdot}1$ V *vs* N.C.E. A sufficient, at least tenfold excess, of the oxidizing agent was used in these experiments. It was ensured that the initial concentration of volatile CCl_4 is not affected by passing nitrogen through the reaction medium. At the potential chosen, an increase in the current was only due to Cr(II) ions. Rate constants of the reactions carried out always under pseudo-first order conditions, k_{obs}, were calculated from the linear dependences, $\log (I_0/I) = f(t)$, where I_0 is the limiting diffusion current of Cr(II) ions at the beginning of the reaction and I is the current at time t. Second order rate constants were obtained by dividing k_{obs} by CCl_4 concentration, the error being ±7%.

RESULTS

Spectra. On addition of CCl_4 to a Cr(II) solution in 50% methanol and 1M-$HClO_4$, the colour of the reaction solution changes from blue *via* red to brown and finally to green. At 298 K, the absorbance first fastly increases practically in the whole region of the spectrum and then it slowly decreases. Difference in the rate of both processes becomes greater on decreasing temperature and at 274 K both phases of the reaction can be conveniently distinguished. The absorption maxima after completion of the first phase lie at 408 and 529 nm in 50% methanol. Absorbance decrease, *i.e.* the decomposition of the red intermediate, is accompanied by gas evolution. The second phase is taking place also under conditions under which the redox reaction of Cr(II) with CCl_4 is practically complete, *i.e.* in the absence of Cr(II) ions. The resulting spectrum corresponds to that of $CrCl^{2+}$ ions ($\varepsilon_{432} = 22$, $\varepsilon_{612} = 19$ l mol^{-1} cm^{-1}).

Chromatography on ion exchangers. Chromatographic separation of Cr(III) complexes formed in the first phase, *i.e.* by the redox reaction of Cr(II) with CCl_4 in 50% methanol containing 0·01 – 1M-$HClO_4$ with the use of the column cooled with ice, has shown the formation of two bands. 0·5M-$HClO_4$ completely eluted and separated the green (identified as $CrCl^{2+}$ ion) and then the red complex. The red complex was identified as the organochromium(III) ion, $CrCCl_3^{2+}$, containing σ-Cr—C bond. Its properties were studied in other work[4]. From the point of view of the mechanism of this redox reaction the relative yields of the $^{2+}$ charged ions formed are of importance. The analysis of chromatographic fractions as to the total amount of chromium was made in both solvents used. When 9·4 . 10^{-3}M-Cr(II)

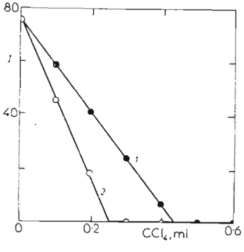

FIG. 1

Polarometric Titration of 10 ml of 9·3 . 10^{-3}M-Cr(II) by 0·1M *1* and 0·2M-CCl_4 *2* in 50% Methanol

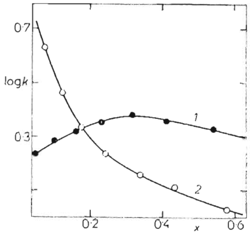

FIG. 2

Dependence of Logarithm of the Rate Constant *k* on the Mole Fraction of Methanol (curve *1*) and of Acetic Acid (curve 2) solution was allowed to react with $(1-2) . 10^{-2}$ M-CCl_4 in 0·1M-$HClO_4$ 50% methanol, the initial yield of $CrCl^{2+}$ (expressed as the number of mol of $CrCl^{2+}$ species formed from 1 mole of the reacted Cr(II)) was close to 0·5. The analysis of the green band obtained by the reaction under the same conditions but in 50% acetic acid showed that 44–49% of the reacted chromium is present in the form of $CrCl^{2+}$ after the first stage of the reaction is completed, *i.e.* the redox reaction of Cr(II) with CCl_4. These results, along with the observed stoichiometry, allow to describe the oxidation of Cr(II) ions with tetrachloromethane by Eq. (*A*).

$$2\,Cr^{2+} + CCl_4 = CrCl^{2+} + CrCCl_3^{2+} \qquad (A)$$

Kinetics. Kinetics of the oxidation of Cr(II) ions with tetrachloromethane was followed under following conditions: $[Cr(II)]_0 \sim 10^{-4}$M, $[CCl_4]_0 = (0{\cdot}75 - 3) . 10^{-3}$M, $[HClO_4]$ = 0·01 – 1M, ionic strength 0·01 – 1M, temperature 289 – 313 K, the mole fraction of methanol 0·048 – 0·83 and the mole fraction of acetic acid 0·073 to 0·577. In sufficient excess of tetrachloromethane, the reaction proceeded according to first order kinetics at least to 90% conversion. The k_{obs} *vs* $f[CCl_4]_0$ dependence was linear and passed through the origin. This proves the first order of the reaction in CCl_4 concentration. The rate law is following (Eq. (*1*)).

$$-d[Cr(II)]/dt = 2k[Cr(II)]\,[CCl_4] \qquad (1)$$

$k = 2{\cdot}35\ l\ mol^{-1}\ s^{-1}$ at 293 K in 50% methanol does not depend on H^+ ions concentration and also on ionic strength in the range 0·01 to 1M. The activation parameters determined from the Eyring equation were $\Delta H^{+} = 25{\cdot}2\ kJ\ mol^{-1}$ and $\Delta S^{+} = -146\ J\ mol^{-1}\ K^{-1}$. Similarly, the first order was also confirmed for the reaction in acetic acid. The second order rate constant k equals to $1{\cdot}66\ l\ mol^{-1}\ s^{-1}$ at 293 K (50% acetic acid). The co-solvent affects the reaction rate in different way (Fig. 2). Maximal value of the rate constant in 50% methanol is by 40% higher than the minimal values obtained in 10% and 90% methanol.

DISCUSSION

The first order dependence for the oxidation of Cr(II) ions with CCl_4 in both media excludes the possibility that the rate determining step is a homolytic cleavage of the C—Cl bond in tetrachloromethane, followed by the reactions of its fragments with Cr^{2+} ions, although this would lead to the observed initial Cr(III) products. The stoichiometry determined and the experiments on ion exchangers indicate that the reduction of CCl_4 by $Cr(ClO_4)_2$ in methanol or in acetic acid leads to the formation of only one organochromium(III) ion-$CrCCl_3^{2+}$ (in contradistinction to the reduction[2] of $CHCl_3$ by $CrSO_4$ in dimethylformamide which proceeds through $CrCHCl_2^{2+}$, $CrCH_2Cl^{2+}$ and $CrCH_3^{2+}$).

In the case of tetrachloromethane there is little doubt (the formation of primary $CrCl^{2+}$ product and the composition of activated complex 1 mol Cr(II) and 1 mol CCl_4 being proved) that the rate determining step of the reaction is transfer of the chlorine atom from CCl_4 to Cr(II) *via* inner sphere mechanism, *i.e.* by the reaction (*B*), which is followed by a fast association of $\dot{C}Cl_3$ with another Cr(II) ion.

$$Cr^{2+} + Cl—CCl_3 \rightarrow [Cr—Cl—CCl_3^{2+}]^{\ddagger} \rightarrow CrCl^{2+} + \dot{C}Cl_3 \qquad (B)$$

In both media, H_2O-CH_3OH-$HClO_4$ and H_2O-CH_3COOH-$HClO_4$, the identical stoichiometric coefficients, reaction orders and yields of $CrCl^{2+}$ ions were established. This shows that the structure of the Cr—Cl—C bridge is retained in both media. The dependence of the rate constant on the co-solvent mole fraction is, however, different. In the reaction of ion with neutral molecule, the rate constant should increase with decreasing permitivity of medium[7]. This prediction does not agree with our results. This indicates the possibility of specific interactions between solvent molecules and the reactants. A relative, high negative activation entropy further shows that the activated complex is strongly solvated by water and/or by methanol molecules. For that reason the addition of acetic acid decreases the rate of the redox reaction of Cr(II) ions with tetrachloromethane.

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