# AN INNER SPHERE REDOX REACTION OF Cr(II) IONS WITH HALOGENOACETIC ACIDS. STOICHIOMETRY, KINETICS, AND MECHANISM

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The stoichiometry and kinetics of oxidation of Cr(II) ions with monochloro-, monobromo-, and monoiodoacetic acid have been investigated in an aqueous solution of perchloric acid. In all the reactions 2 moles of Cr(II) were consumed per 1 mol of the acid. The primary Cr(III) products are halogenopentaaquochromium(III) ions (up to 50% of the total amount of the Cr(III) products). Redox reactions are first order in concentration of each reactant. The rates of oxidation of Cr(II) ions with halogenoacetic acids decreasing in the order I > Br > Cl are $1·9 . 10^3 : 2·1 . 10^2 : 1$. The reaction mechanism has been proposed which involves halogen transfer from the monohalogenoacetic acid to Cr(II) as the rate determining step. This transfer proceeds *via* the bridged activated complex $[(H_2O)_5CrXCH_2COOH)^{2+}]^{\neq}$.

The inner sphere mechanism of redox reactions of Cr(II) ions with halogen-containing compounds in solutions is exemplified mainly by halogen transfer reactions. The structure of the Cr(III) complexes formed depends upon the mechanism of a given reaction. $Br_2$ and $I_2$ oxidize $Cr_{aq}^{2+}$ ions by inner sphere mechanism[1] and the products are $Cr(H_2O)_5X^{2+}$ (X = Br and I). The oxidation with $Cl_2$ results in formation of $Cr(H_2O)_5Cl^{2+}$, $Cr(H_2O)_6^{3+}$ and a certain amount of binuclear Cr(III) complexes[1,2]. Similarly, reactions of $Cr_{aq}^{2+}$ ions with halogen anion radical $I_2^-$ and $Br_2^-$ proceed exclusively by inner sphere mechanism, the reaction with $Cl_2^-$ taking place to the same extent by both outer and inner sphere path[3]. The reduction of alkyl halogenides[4] and benzyl halogenides[5] by Cr(II) ions are analogous to inner sphere reductions of $Co(NH_3)_5X^{2+}$, $Cr(NH_3)_5X^{2+}$ or $Cr(H_2O)_5X^{2+}$ by Cr(II) ions[6] (X = halogen).

In the preliminary study[7] of the redox reaction of Cr(II) with monochloroacetic acid the interfering effect of this reaction upon kinetics of the reduction of monochloroacetopentamminecobalt(III) complexes with Cr(II) ions has been investigated. Chlorine transfer to coordination sphere of the primary Cr(III) complexes has been postulated based on kinetic studies of the oxidation of Cr(II) ions with trichloro-[8] and dichloroacetic acid[9]. Until now, the reaction paths for the reaction of Cr(II) with monochloro-, monobromo-, and monoiodoacetic acids have not been determined. This was the aim of the present study.

## EXPERIMENTAL

*Chemicals.* All stoichiometric and rate measurements were carried out in nitrogen atmosphere. The nitrogen for lamps was purified by passing through the washing bottle containing Cr(II) ions which were prepared by the reduction of $1M$-$Cr(ClO_4)_3$ solution with zinc amalgam. Reaction solutions were prepared fresh each day from analytically pure chemicals and were stored in the dark and cold. Aqueous solutions of $Cr(ClO_4)_2$ were prepared by dissolving the excess metallic chromium (99·999%, Koch-Light) in perchloric acid of an appropriate concentration (usually 0·1–$1M$) for 12—14 h at room temperature and were stored under nitrogen. Before dissolving, the chromium was activated by $6M$-HCl. The amount of Cr(III) impurities in these solutions was determined polarographically from the ratio of the limit difussion anodic current of Cr(II) ions ($E_{1/2} = -0·36$ V *vs* N.C.E. in $1M$-$HClO_4$) to the height of the cathodic wave of Cr(III) ($E_{1/2} = -0·98$ V *vs* N.C.E. in $1M$-$HClO_4$). The average content of Cr(III) impurities in the reaction solution of Cr(II) ions was 5—6 per cent.

*Analyses.* The Cr(III) complexes formed were separated from the reaction system by ion exchanger chromatography. The column ($10 \times 1$ cm) was packed with Dowex 50 W-X2 (200—400 mesh) in the $H^+$ form. The redox reactions of Cr(II) with monoiodoacetic and monobromoacetic acids were found to be complete in several minutes in $0·01M$—$1M$-HClO$_4$ at room temperature with initial concentrations of the reactants equaling to c. 0·2M, whereas in the case of monochloroacetic acid Cr(II) ion had to be reacted with the acid for 2—3 h, even with $ClCH_2COOH$ concentration by one order of magnitude higher. The mixture was then diluted with water to decrease ionic strength below 0·1M. Approximately $10^{-3}$ mol of Cr(III) was introduced into the cation exchanger column. The 2+ charged Cr(III) complexes were eluted usually with 0·5M-$HClO_4$ and the hexaaquochromium(III) ions with $1M$-$HClO_4$. Under these conditions complexes bearing the higher charge, such as $(CrOH)_2^{4+}$, were fixed in the top of the column and could be removed only by using $4M$-$HClO_4$. Elution times varied from 20 to 60 min. The Cr(III) fractions collected were analysed spectrophotometrically (Specord UV VIS, Zeiss, Jena). The total content of chromium in these fractions was determined spectrophotometrically, too, after oxidation to chromate with an alkaline solution of hydrogen peroxide, by measuring the absorbance at 372 nm ($CrO_4^{2-}$, $\varepsilon_{372} = 4815$ l mol$^{-1}$ cm$^{-1}$).

*Kinetics.* Kinetics of the oxidation of Cr(II) ions by $XCH_2COOH$ (X = Cl, Br, and I) in aqueous $HClO_4$ has been followed polarographically. The time dependence of the limit anodic diffusion current of Cr(II) at a constant potential of 0·0 V (−0·2 V in the reaction of $ICH_2COOH$) against N.C.E. has been monitored. Polarographic measurements were carried out on LP 7 instrument (Laboratorní přístroje, Prague). The normal calomel electrode was used as the reference and mercury dropping electrode (time of drops 4 s, flow rate 1·85 mg s$^{-1}$ at the 64 cm mercury reservoir height and at zero potential) has been used as the indicator. The reaction flask was a thermostatted Kalousek polarographic cell. The removal of oxygen and the mixing of solutions was achieved by bubbling nitrogen through the solution. The height of the limit current of Cr(II) ions was proportional to their concentration and did not change with time in the absence of $XCH_2COOH$. Of all the reactants and products, only Cr(II) ions are responsible for the current at the potential chosen (for $ClCH_2COOH$ $E_{1/2} = -1·61$ V, for $BrCH_2COOH$ $E_{1/2} = -0·70$ V and for $ICH_2COOH$ $E_{1/2} = -0·37$ V, all against N.C.E. in $1M$-$NaClO_4$). In all kinetic measurements oxidizing agents were used in excess and rate constants were calculated from the integrated form of the first order kinetic equation (Eq. (*1*)) where $I_0$ is

$$\log (I_0/I) = k_{obs}t/2·303 \qquad (1)$$

the limit diffusion current of Cr(II) at the beginning of the reaction and $I$ is the current at the

time $t$. The rate constant of the second order reaction $k$ was obtained by dividing $k_{obs}$ with $XCH_2COOH$ concentration. In some reactions of Cr(II) with monoiodoacetic acid it was necessary to make allowance for a decrease in the concentration of $ICH_2COOH$ according to the stoichiometric equation. At the same time, $\log I_0/I = f(t)$ dependences were linear. The reactions were followed usually over 3 half times. The recorded values of rate constants are the average of 3 measurements. $k_{obs}$ was determined with an accuracy of $\pm 5\%$ (7% for $ICH_2COOH$).

## RESULTS

*Stoichiometry.* The stoichiometry of redox reactions of Cr(II) ions with monobromo- and monoiodoacetic acids was determined by polarometric titrations. From the graphical dependence of the height of the limit diffusion current of Cr(II) ions after completion of the redox reaction upon the amount of the titrating agent it follows that 2 mol of Cr(II) are consumed per 1 mol of monobromoacetic acid. The increase in the Cr(III) wave at $-1.2$ V against N.C.E. and the decrease in the wave corresponding to monoiodoacetic acid at $-0.47$ V against N.C.E. has been utilized to determine the stoichiometry of the Cr(II) + $ICH_2COOH$ reaction. Two moles of Cr(III) are produced by this reaction per 1 mol of the monoiodoacetic acid reacted. The stoichiometry of the Cr(II) + $ClCH_2COOH$ reaction has been determined from a decrease in the height of the Cr(II) wave at 0 V *vs* N.C.E. (because of relatively slow rate of the reaction), Cr(II) being used in excess together with the known amount of monochloroacetic acid. Polarographic analysis of unreacted Cr(II) has shown that 2 mol of Cr(II) reacted with 1 mol of $ClCH_2COOH$.

Chromatographic separation of Cr(III) products of redox reactions of Cr(II) with $XCH_2COOH$ (X = Cl, Br, and I) has revealed that two Cr(III) complexes are formed which are distinctly separated from one another by using $0.5M$-$HClO_4$. The green bands (the $2+$ charge) were eluted first, followed by the red bands (the $2+$ charge). However, in the Cr(II) + $ClCH_2COOH$ reaction a violet-blue band (the $2+$ charge) has been separated in place of the red fraction (which was detected only in the initial stage of the reaction). The position and intensity of absorption maxima of green fractions (Fig. 1) prove formation of inner sphere reaction products of the type $Cr(H_2O)_5X^{2+}$. The absorption spectra of the red Cr(III) products of redox reactions of Cr(II) with monoiodo- and monobromoacetic acids have been identical ($\varepsilon_{272} = 3876$, $\varepsilon_{417} = 89.5$, and $\varepsilon_{553} = 40.01 \, mol^{-1} \, cm^{-1}$). Their pattern indicates formation of an organochromium(III) complex with the Cr—C bond[9,10]. The violet-blue product of the Cr(II) + $ClCH_2COOH$ reaction is likely produced by consecutive reactions of the primary organochromium(III) complex under given experimental conditions. Certain amounts of $Cr(H_2O)_6^{3+}$ and binuclear Cr(III) complexes have been found by the analysis of the reaction products arising from the Cr(II) + $ClCH_2COOH$ reaction. The primary products of the aquation of the complexes studied in an aqueous solution of perchloric acid and an atmosphere of nitrogen are hexaaquochromium(III) ions.

In further experiments we have determined the yields of halogenopentaaquo-chromium(III) and organochromium(III) complexes. The results obtained are summarized in Table I. The redox reactions were allowed to proceed for more than 7 half times (c. 2 min with $ICH_2COOH$, 6 min with $BrCH_2COOH$, and 2·5 h with

TABLE I

Yields of Cr(III) Products of the $Cr^{2+} + XCH_2COOH$ Reactions

| X | $[Cr^{2+}]_0$ | $[XCH_2COOH]_0$ | $[HClO_4]_0$ | Yields[a] | | Inner sphere path, % |
|---|---|---|---|---|---|---|
| | | | | $CrX^{2+}$ | $CrCH_2COOH^{2+}$ | |
| Cl | 0·12 | 1·5 | 0·5 | 19[b] | . | >50 |
| | 0·12 | 1·5 | 0·5 | 21 | | |
| Br | 0·19 | 0·4 | 0·5 | 47[c] | 48 | 98 ± 4 |
| | 0·10 | 0·4 | 0·5[d] | 48[c] | | |
| | 0·19 | 0·4 | 0·5[e] | 48[c] | | |
| | 0·10 | 0·4 | 0·5[f] | 47[c] | | |
| I | 0·21 | 0·4 | 1·0 | 44[g] | 48 | 99 ± 7 |
| | 0·12 | 0·4 | 0·5 | 32 | | |
| | 0·19 | 0·4 | 0·2 | 15 | | |

[a] Yields are expressed in per cent of the total Cr(III) yields. [b] The redox reaction was interrupted after 2 half times; after allowance for the unreacted Cr(II), the yield of $CrCl^{2+}$ was c. 25%. [c] By 1% higher when allowance is made for the aquation of $CrBr^{2+}$. [d] 0·8M-$Cl^-$. [e] 0·8M-$Br^-$. [f] 0·8M-$I^-$. [g] The yield after correction for the aquation of $CrI^{2+}$ is 49·5%.



$\varepsilon$, l.$M^{-1}$cm$^{-1}$
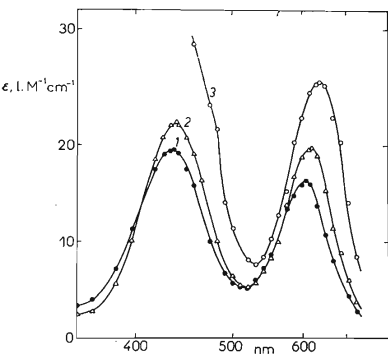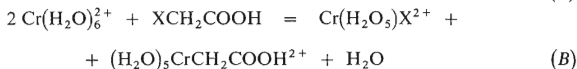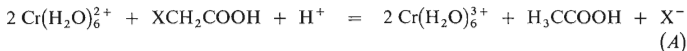
FIG. 1

Absorption Spectra of First Fractions Separated on an Ion Exchanger from the $Cr^{2+} + XCH_2COOH$ Reactions after Redox Reaction Has Been Completed

*1* X = Cl, *2* X = Br, *3* X = I.

$ClCH_2COOH$ at 298 K). In calculations the alowance was made for the impurification of the stock solution of Cr(II) ions by Cr(III) ions (6%). At optimal separation 96—98% of the total amount of chromium were recovered. As follows from Table I, 0·5 mol of $Cr(H_2O)_5X^{2+}$ (X = Br, I) and 0·5 mol of $[(H_2O)_5CrCH_2COOH]^{2+}$ are produced per 1 mol of Cr(II). This proportion is not influenced even by the presence of $Cl^-$, $Br^-$, and $I^-$ ion in the Cr(II) + $BrCH_2COOH$ system.

The above results show that the overall stoichiometry of Cr(II) + $XCH_2COOH$ (X = Cl, Br, and I) reactions in an aqueous solution of perchloric acid is described by Equation $(A)$ and the stoichiometry of the proper redox reaction

$$2\,Cr(H_2O)_6^{2+} + XCH_2COOH + H^+ = 2\,Cr(H_2O)_6^{3+} + H_3CCOOH + X^-$$
$$(A)$$

$$2\,Cr(H_2O)_6^{2+} + XCH_2COOH = Cr(H_2O_5)X^{2+} +$$
$$+ (H_2O)_5CrCH_2COOH^{2+} + H_2O \qquad (B)$$

can be depicted by Equation $(B)$ for X = Br, I, and likely also for X = Cl.

*Kinetics.* Reactions of Cr(II) with monochloro-, monobromo-, and monoiodo-acetic acid proceeded under first order kinetic conditions, with an excess of $XCH_2$. $.COOH$ (X = Cl, Br, and I). (For each system the initial $XCH_2COOH$ concentration varied about 8-fold, starting with 200-, 20 and 6-fold excess for X = Cl, Br, and I, respectively). The reaction course obeyed first order kinetics at least to 90% conversion. Rate constants $k_{obs}$, which were calculated from Eq. (1), increased linearly with increasing concentration of the oxidizing agents (Fig. 2) which proves that the reactions are first order in monohalogenoacetic acids. The rate law can be there-
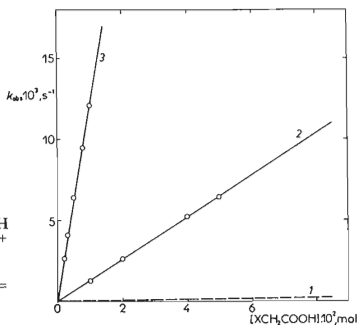
Fig. 2

First Order Dependence upon $XCH_2COOH$ for the Reaction of the Acid with $Cr^{2+}$ in 0·5M-$HClO_4$

1 X = Cl (extrapolated). 313·2 K, 2 X = = Br, 298·2 K, 3 X = I, 298·2 K.

fore written in the following form $\left(\text{Eq. } (2)\right)$ where X is

$$-d[\text{Cr(II)}]/dt = k[\text{Cr(II)}] \text{ I. } [\text{XCH}_2\text{COOH}] \qquad (2)$$

Cl, Br, and I, and $[\text{XCH}_2\text{COOH}]$ denotes the total concentration of monohalogeno-acetic acid (under conditions used $[\text{Cr(II)}] = [\text{Cr}^{2+}]$). The results of some kinetic measurements are presented in Table II. The rate constant $k$ does not depend upon ionic strength (which was adjusted by $\text{NaClO}_4$), upon $[\text{X}^-]$ (X = Cl, Br) in the $0-0.4\text{M}$ region, and upon $[\text{H}^+]$ ($0.01-0.5\text{M}$ range for X = Br and $0.4-0.9\text{M}$ range for X = I). The rate constant $k$ for the Cr(II) + $\text{ClCH}_2\text{COOH}$ system decreases with increasing $\text{H}^+$ concentration, beyond the experimental error. Providing that $\text{ClCH}_2\text{COOH}$ is dissociated $\left(K_D = 1.55 \cdot 10^{-3} \text{ mol l}^{-1}\right)$ is the highest value of dissociation constant of all the acids studied[11]) and assuming that the reaction of Cl. $.\text{CH}_2\text{COO}^-$ ($k_1$) and $\text{ClCH}_2\text{COOH}$ ($k_2$) with Cr(II) ions are rate determining, the dependence of the rate constant $k$ on $[\text{H}^+]$ takes the following form (3) in the region

TABLE II
Rate Constants for the $\text{Cr}^{2+} + \text{XCH}_2\text{COOH}$ Reactions

| X | Temperature | $[\text{HClO}_4]_0$ | $10^2 k$, l mol$^{-1}$ s$^{-1}$ |
|---|---|---|---|
| Cl[a] | 303.9 | 0.01 | 0.105 |
| | 303.9 | 1.0 | 0.091 |
| | 313.3 | 0.01 | 0.182 |
| | 313.3 | 1.0 | 0.141 |
| | 323.7 | 0.01 | 0.330 |
| | 323.7 | 1.0 | 0.265 |
| Br[b] | 288.5 | 0.5 | 8.08 |
| | 298.2 | 0.01 | 13.5 |
| | 298.2 | 0.5 | 13.1 |
| | 311.6 | 0.5 | 26.3 |
| | 320.8 | 0.5 | 41.7 |
| I[c] | 280.6 | 0.9 | 56.4 |
| | 286.1 | 0.9 | 68.2 |
| | 298.2 | 0.4 | 115 |
| | 298.2 | 0.9 | 107 |
| | 303.1 | 0.9 | 122 |

[a] Ionic strength 1M, $[\text{ClCH}_2\text{COOH}]_0 = 1\text{M}$, $[\text{Cr(II)}]_0 = 1.5 \cdot 10^{-3}\text{M}$.  [b] Ionic strength 0.5M, $[\text{BrCH}_2\text{COOH}]_0 = 4 \cdot 10^{-2}\text{M}$, $[\text{Cr(II)}]_0 = 2 \cdot 10^{-3}\text{M}$.  [c] Ionic strength 0.9M, $[\text{ICH}_2\text{COOH}]_0 = 10^{-2}\text{M}$, $[\text{Cr(II)}]_0 = (0.8-1) \cdot 10^{-3}\text{M}$.

where $[H^+]/K_D \gg 1$. From the $k$ vs $[H^+]^{-1}$ plot the rate constant $k_2$ equaling to $1\cdot54$ . $.\ 10^{-3}$ l mol$^{-1}$ s$^{-1}$

$$k = \frac{k_1 K_D}{[H^+]} + k_2 \qquad (3)$$

is obtained from the intercept on the $k$ axis; the $k_1$ value which was estimated from the slope and $K_D$ value equaled to c. $1\cdot6$ . $10^{-3}$ l mol$^{-1}$ s$^{-1}$ at a temperature of 313·3 K.

The graphical dependence of $-\log kh/\bar{k}T$ upon $T^{-1}$ was linear in all cases. The activation parameters for Cr(II) + XCH$_2$COOH reactions which are presented in Table III were determined on the basis of the Eyring absolute reaction rate relations.

## DISCUSSION

The activated complex for the oxidation of Cr(II) ions with XCH$_2$COOH (X = Cl, Br, and I) contains one molecule of Cr(II) and one molecule of the oxidizing agent. As the stoichiometry of the redox reaction differs from that of the activation step, several consecutive steps must be involved in the reaction mechanism. The formation of Cr(H$_2$O)$_5$X$^{2+}$ and $[(H_2O)_5CrCH_2COOH]^{2+}$ products *via* two step mechanism in which the first step is homolysis of XCH$_2$COOH that is followed by fast capture of $\dot{C}H_2COOH$ and X by Cr(II) ions (Cr$^{2+}$ + $\dot{C}H_2COOH \rightarrow$ (CrCH$_2$COOH)$^{2+}$ and Cr$^{2+}$ + X $\rightarrow$ CrX$^{2+}$) is clearly excluded by the form of the rate law which indicates the first order dependence upon Cr(II) concentration. Experimental evidence requires a direct attack of Cr$^{2+}$ onto the halogen of monohalogenoacetic acid.

Kinetic and product analyses show further that the rate determining step is the inner sphere redox reaction (Eq. (C)).
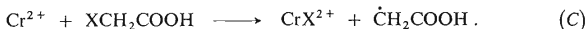
$$Cr^{2+} + XCH_2COOH \longrightarrow CrX^{2+} + \dot{C}H_2COOH . \qquad (C)$$

TABLE III
Activation Parameters for the Cr$^{2+}$ + XCH$_2$COOH Reactions

| X | $\Delta H^{\ddagger}$, kJ mol$^{-1}$ | $\Delta S^{\ddagger}$, J K$^{-1}$ mol$^{-1}$ |
|---|---|---|
| Cl | $42\cdot6 \pm 3$ | $-163 \pm 12$ |
| Br | $36\cdot8 \pm 2\cdot4$ | $-137\cdot5 \pm 8$ |
| I | $22\cdot6 \pm 3$ | $-169 \pm 12$ |

This reaction is followed by fast interaction with another $Cr^{2+}$ ion (Eq. ($D$)).

$$Cr^{2+} + \overset{\cdot}{C}H_2COOH \xrightarrow{\text{fast}} CrCH_2COOH^{2+} . \qquad (D)$$

Such a mechanism involves rate determining transfer of the halogen of mono-halogenoacetic acid to Cr(II) *via* the bridged activated complex $[(H_2O)_5CrXCH_2.COOH)^{2+}]^{\neq}$. Our findings indicate that the yields of primary $Cr(H_2O)_5X^{2+}$ and $[(H_2O)_5CrCH_2COOH]^{2+}$ products are close to 50% of the total amount of Cr(III) products in the oxidation of Cr(II) with $BrCH_2COOH$ and $ICH_2COOH$. Therefore, the oxidation of Cr(II) with $XCH_2COOH$ (X = Br and I) is exclusively inner sphere process. The yield of $Cr(H_2O)_5Cl^{2+}$ is markedly lower than 50%, similarly to the yield of $Cr(H_2O)_5I^{2+}$ at lower concentrations of $H^+$. The ratio of the rate constants of Cr(II) + $XCH_2COOH$ reactions to the rate constants obtained for uncatalysed aquation of $Cr(H_2O)_5X^{2+}$ complexes (X = I, Br, and Cl) (ref.[12,13]) is $1 \cdot 4 . 10^4$ : : $4 \cdot 2 . 10^4 : 2 \cdot 2 . 10^3$ at 298 K. It is seen that the most suitable conditions for quantitative yields of $CrX^{2+}$ exist in the redox reaction with $BrCH_2COOH$ and that consecutive reactions of $Cr(H_2O)_5X^{2+}$ complexes are slow enough compared to redox reaction that they do not influence substantially the product distribution of redox reaction at high $H^+$ concentrations. However, under experimental conditions used by us (at $[ClCH_2COOH]_0 = 1 \cdot 5M$, $[Cr(II)]_0 = 0 \cdot 12M$, the reaction time requested is c. 2·5 h) the decrease in the yields of $Cr(H_2O)_5Cl^{2+}$ can be caused by the $Cr^{2+}$-catalysed dissociation of $CrCl^{2+}$ (the higher relative yield of $CrCl^{2+}$ at the shorter reaction time — see[b] in Table I). The formation of $CrX^{2+}$ as primary products of Cr(II) oxidation confirms the tendency to capture oxidizing agents (or parts of them) within the coordination sphere of the Cr(III) products formed. In addition to this, the above assumption is in accordance with the ability of Cr(II) salts to reduce halogen and nitro groups while carbonyl groups of organic compounds are not attacked[14]. It is worthy of note that the reaction (C) is analogous to the oxidation of Cr(II) ions with trichloro-[8] and dichloroacetic acid[9].

The sequence of the rates of reduction of chloroacetic acids by Cr(II) ions is trichloro-, > dichloro- > monochloroacetic acid $(1 \cdot 5 . 10^4 : 3 \cdot 2 . 10^2 : 1)$. The order for monohalogenoacetic acids is I > Br > Cl $(1 \cdot 9 . 10^3 : 2 \cdot 1 . 10^2 : 1)$. The reactivity of halogenoacetic acids parallels an inner sphere reduction of various alkyl halogenides by Cr(II) ions[4]. Reactions of Cr(II) with halogenoacetic acids are characterized by relatively high negative values of activation entropy $\Delta S^{\neq}$ which is approximately the same for the whole series under study. This indicates that the transition state has ordered structure and means that the rate order observed at 298 K will be preserved over broad temperature range. Hence, observed differences in the rate constants of reactions of different halogenoacetic acids reflect above all difference in $\Delta H^{\neq}$ values. The low activation enthalpies comport the mechanism which involves

only small changes in reorganization of hydration spheres prior to halogen transfer process.

In redox reactions of $Co(NH_3)_5X^{2+}$, $Cr(NH_3)_5X^{2+}$, and $Cr(H_2O)_5X^{2+}$ complexes with $Cr^{2+}$ ions the so-called normal reactivity order $(I > Br > Cl > F)$ has been established[6,15]. In these reactions the influence of bond formation is regarded to be less important compared to bond breaking or to the permeability of bridge ions[16]. If we compare the ratio of rate constants (rate order) of the reactions of Cr(II) with $Cr(NH_3)_5X^{2+}$, Cr(II) with $Co(NH_3)_5X^{2+}$, and Cr(II) with $XCH_2COOH$ it becomes evident that the nature of the central atom of the oxidizing agent affects the capability of transferring electron through the bridge ligand. The use of the same approach together with data reported for reactions of Cr(II) with alkyl halogenides[4], benzyl halogenides[5] and monohalogenoacetic acids (this work) leads to the conclusion that in reactions of the type $RCH_2X + Cr(II)$ (which exhibit substantially higher values of the $k_X/k_{Cl}$ ratio for X = Br and I) the same factors (may be the C—X bond strenght) limit the rate of halogen transfer to Cr(II) ion.

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