MECHANISM OF OXIDATION OF Cr(II) IONS BY CHLOROFORM, BROMOFORM, AND IODOFORM

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The kinetics and mechanism of oxidation of Cr(II) ions by haloforms were studied in H_2O--CH_3OH-$HClO_4$ system, in the case of bromoform also in H_2O-CH_3COOH-$HClO_4$ system. Six mol of Cr^{2+} ions is consumed in the oxidation–reduction reaction per one mol of CHX_3, the final organic product is methane. The primary Cr(III) products are CrX^{2+} ions and $[CrCHX_2^{2+}]$ organochromic complexes. The oxidation–reduction reactions are 1st order with respect to each reactant, the rate constants of the 2nd order reaction, independent of the H^+ ion concentration and the ionic strength, decrease in the order $k_I > k_{Br} > k_{Cl}$. The inner-sphere mechanism is suggested for the electron transfer; the effect of the C—X bond cleavage is more significant than the effect of the Cr—X bond formation and controls the rate of the halogen atom transfer from the haloform to Cr(II).

An inner-sphere type of electron transfer mechanism has been postulated for oxidation–reduction reactions of pentamminehalogenidecobalt(III) complexes with Cr(II) ions, based on a kinetic determination of the composition of the activated complex and on the fact that pentaquohalogenidechromium(III) complexes are formed as the primary products rather than the thermodynamically more stable combination of hexaquochromium(III) and halide ions[1].

As is well known, requisite for the inner-sphere mechanism is the presence of a lone electron pair at the atom or group that is to act as the bridge. An analogy can be therefore expected to be between reactions of $[Co(NH_3)_5X]^{2+}$ with Cr^{2+} ions and those of Cr(II) with haloforms. However, it must be taken into account that the oxidants differ in their charges, and in the case of haloforms the one-electron change does not lead to stable products. One of σ-bonded organochromium(III) complexes known for a long time, $[CrCHCl_2]^{2+}$, has been prepared by Anet[2] by reduction of chloroform with chromous perchlorate. The qualitative study[3] of oxidation of Cr(II) ions by chloroform, bromoform, and iodoform, respectively, indicated that methane could be expected as the resulting organic product in DMF–H_2O system if chromous sulphate is used as the reductant. On the other hand, Dodd and Johnson[4] were unable to isolate pentaquomethylchromium(III) ion in acetone–water system as a direct precursor of methane in those oxidation–reduction reactions. Reaction of Cr^{2+} with $[CrCH_2I]^{2+}$ gave rise to methane[5,6], whereas direct reaction of Cr^{2+} with $[CrCH_2Cl]^{2+}$ and formation of methylpentaquochromium(III) ion in aqueous solution of perchlorate ions was not observed[7].

In this work we present the results of a kinetic study of the mechanism of oxidation of Cr(II) ions by chloroform, bromoform, and iodoform, respectively, in H_2O–CH_3OH–$HClO_4$ system, for bromoform also in H_2O–CH_3COOH–$HClO_4$ system. Replacement of the halogen in the CHX_3 compounds also offers the possibility, in the case of the inner-sphere mechanism (proved experimentally) to evaluate the role of the bridging halogens in the oxidation–reduction reaction of Cr(II) ions with organic halides.

EXPERIMENTAL

Chemicals and solutions. Solutions of Cr(II) ions were prepared by dissolving excess chromium metal (99·999%, Koch Light) in $HClO_4$ solution (usually 0·1 – 1M) under nitrogen. The content of Cr(III) impurities in the solutions was determined polarographically from the ratio of the anodic limiting diffusion current of the 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 the Cr(III) ions ($E_{1/2} = -0{\cdot}98$ V *vs* N.C.E. in 1M-$HClO_4$). The average content of the Cr(III) impurities was 7% with respect to the Cr(II) ion concentration. The other solutions used were prepared from commercial reagent grade chemicals and distilled water. Freshly prepared solutions of halides in methanol were used; chloroform was distilled prior to use.

Analysis. The chromic complexes, resulting as the reaction products, were separated chromatographically on ion exchanger. An ice-cooled column packed with Dowex 50WX2 (200 – 400 mesh) in the H^+ form was employed. Before the chromatographic treatment, the ionic strength of the solution of the products was adjusted below 0·1M with distilled water. The Cr(III) complexes carrying 2+ charge were eluted with 0·5M or 1M-$HClO_4$, those carrying 3+ charge with 2M-$HClO_4$. The column was freed from the binuclear Cr(III) complex possessing 4+ charge, which is a product of possible oxidation of Cr(II) by atmospheric oxygen (if Cr(II) was present in the reaction mixture in a stoichiometric excess), by using 4 – 5M-$HClO_4$. The primary and the final reaction products were separated. The ratio of the initial concentrations $[Cr(II)]_0 : [CHX_3]_0$ was 1 : 30 through 10 : 1. The various Cr(III) fractions were eluted in 10 – 40 min. After the separation, the Cr(III) products were identified by evaluating their absorption spectra scanned on a Specord UV-VIS spectrophotometer (Carl Zeiss, Jena). The total chromium concentration was determined spectrophotometrically at 372 nm (ε 4830 l mol^{-1} cm^{-1}) after oxidation to chromate by using a 0·05M solution of hydrogen peroxide in 1·5M-NaOH.

The gaseous products were identified on a mass spectrometer interfaced to a gas chromatograph. A System MAT 111 Varian GC/MS apparatus was employed. Helium served as the carrier gas, PORAPAK-Q 80/100 mesh was used as the column packing.

Stoichiometry. Basically the stoichiometry of the reaction of Cr(II) with $CHCl_3$, $CHBr_3$, and CHI_3, respectively, was determined *via* biamperometric titration. The limiting current, proportional to the Cr(II) ion concentration, was measured at 0 V *vs* N.C.E. Both possible procedures, *i.e.* titration of Cr(II) ions with the haloforms and *vice versa*, were applied.

The amount of the gaseous product formed (as well as the kinetics of its evolution) was monitored in a measuring apparatus allowing measurements of gas volumes in inert atmosphere at constant pressure, the reaction mixture being stirred with an electromagnetic stirrer.

Kinetics. Kinetics of oxidation of Cr(II) ions by chloroform, bromoform, and iodoform, respectively, in H_2O–CH_3OH–$HClO_4$ system (for $CHBr_3$ also in H_2O–CH_3COOH–$HClO_4$ system) was examined polarographically (LP 7e polarograph, Laboratorní přístroje) by measuring the time dependence of the limiting diffusion anodic current of Cr(II) ions at a constant potential of 0 V *vs* N.C.E., where the current is sensitive to the Cr(II) ions only. A sufficient excess of the oxidant was used; the initial concentration of the volatile chloroform and bromoform was unaffected by nitrogen bubbling through the reaction system. The rate constants k_{obs} of the reactions of Cr(II) with $CHCl_3$ or $CHBr_3$, conducted under conditions of the pseudo-first order, were evaluated from the linear dependences $\log (I_0/I) = f(t)$, where I_0 and I are the limiting currents at the beginning of the reaction and in the time t, respectively. The rate constants of the reaction of Cr(II) with $CHCl_3$ measured using mercury dropping electrode were obtained with an error of ±14%; the error was reduced to ±6% on employing rotating platinum electrode. In the system of Cr(II) with $CHBr_3$ the error was ±5%. The polarographic technique provided also the lower limit of the rate constant value for the fast reaction of Cr(II) with CHI_3. The maximum possible value of the reaction halflife for this reaction, which was assumed to be 1st order with respect to the concentrations of the two reactants, was determined by gradual lowering of the equivalent concentrations of both Cr(II) ions and iodoform.

RESULTS

Stoichiometry of the oxidation–reduction reactions. The final products of oxidation of Cr(II) ions by haloforms in H_2O–CH_3OH–$HClO_4$ system are methane, hexaquochromic ions, and halide ions, in accordance with the stoichiometric equation

$$CHX_3 + 6\,Cr^{2+} + 3\,H^+ = CH_4 + 6\,Cr^{3+} + 3\,X^- . \qquad (A)$$

The validity of this equation was corroborated by the following results. The ratio of the number of mol of reacted Cr(II) ions to the number of mol of reacted haloform, determined by amperometric titrations (see Fig. 1 for the reaction with $CHBr_3$), lay in the range of 5·7–6·25 for $CHCl_3$, 5·42–6·17 for $CHBr_3$, and 6·1 for CHI_3.

Reaction mixtures with the ratio $[Cr(II)]_0 : [CHX_3]_0 = 10 : 1$ were prepared for analysis of the gaseous products. The gas evolution was fastest in the reaction with iodoform for identical concentrations of the reactants. The gas chromatographic and mass spectrometric analyses revealed that methane was the single gaseous product. The ratio of the number of mol of the formed methane to the number of mol of the reacted haloform was determined volumetrically to be 0·96–1·02 for all the three systems in question.

The chromic complex possessing 3+ charge was separated quantitatively by chromatographic treatment on ion exchanger and identified as hexaquochromic ion. 10^{-3} mol $CHBr_3$ in reaction with Cr(II) ions gave $5{\cdot}78 \cdot 10^{-3}$ mol Cr^{3+} for the $[Cr(II)]_0 : [CHBr_3]_0$ ratio 10 : 1.

Kinetics of the oxidation–reduction reactions. The rate constants k_{obs}, determined graphically from the linear dependences $\log (I_0/I) = f(t)$, increased linearly with the haloform concentration, the straight line passing through the origin. This bears out the validity of the rate equation

$$-\mathrm{d}[\mathrm{Cr(II)}]/\mathrm{d}t = k[\mathrm{Cr(II)}]\,[\mathrm{CHX_3}]\,. \qquad (1)$$

The rate constants obtained are $k = 8{\cdot}3\,.\,10^{-2}\ \mathrm{l\,mol^{-1}\,s^{-1}}$ at 289·8 K for $CHCl_3$ in 50% CH_3OH and $k = 4{\cdot}3\ \mathrm{l\,mol^{-1}\,s^{-1}}$ at 298 K for $CHBr_3$ in 50% CH_3OH; they are independent of the proton concentration in the region of 0·02 – 1M-$HClO_4$ and of the ionic strength in the region 0·1 – 1M. For CHI_3, $k^{295} \geqq 2\,.\,10^3\ \mathrm{l\,mol^{-1}\,s^{-1}}$. The following activation parameters were obtained from the temperature dependences of the rate constants by using the Eyring equation: $\Delta H^{\neq} = 29{\cdot}9 \pm 4{\cdot}1\ \mathrm{kJ\,mol^{-1}}$, $\Delta S^{\neq} = -189 \pm 14\ \mathrm{J\,K^{-1}\,mol^{-1}}$ for chloroform and $\Delta H^{\neq} = 24{\cdot}4 \pm 2\ \mathrm{kJ\,mol^{-1}}$, $\Delta S^{\neq} = -166 \pm 7\ \mathrm{J\,K^{-1}\,mol^{-1}}$ for bromoform. The reaction orders with respect to the reactants were not affected by replacing methanol with acetic acid as the co-solvent in the reactions. The rate constant in acetic acid-containing system is lower than in methanolic system, the value decreasing monotonically with increasing concentration of the acid. On the other hand, the dependence of the rate constant on the mole fraction of methanol attains its maximum for the mole fraction $x_{CH_3OH} = 0{\cdot}15$ (Fig. 2).

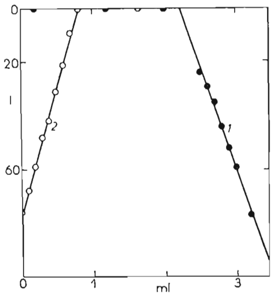

FIG. 1

Amperometric Determination of Stoichiometry of the Reaction of Cr(II) with Bromoform

Titration: *1* 10 ml of 0·01M-$CHBr_3$ with 0·25M-Cr(II), *2* 10 ml of 0·025M-Cr(II) with 0·05M-$CHBr_3$. System of 1M-$HClO_4$, 50% CH_3OH.

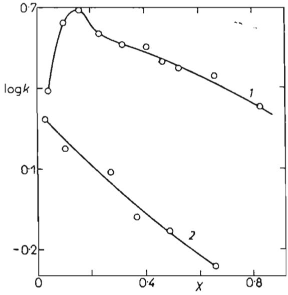

FIG. 2

Dependence of log *k* on the Mole Fraction of Methyl Alcohol or Acetic Acid in the Reaction of Cr(II) with Bromoform

1 CH_3OH, 298·2 K, *2* CH_3COOH, 292·8 K.

Distribution of the primary products. The yields of the CrX^{2+} primary products are of prime importance for the determination of the mechanism of the oxidation–reduction reaction in question. Among the expected intermediate products were also organochromic complex cations $[CrCHX_2]^{2+}$, $[CrCH_2X]^{2+}$, isolated by Dodd and Johnson[4]. These red complexes were eluted from the ion exchanger column more slowly than the green CrX^{2+} complexes. Attempts to isolate the $[CrCH_3]^{2+}$ complex, as the precursor of methane, were successful in the following reaction conditions: 10^{-2}M-$CHBr_3$, 10^{-1}M-Cr(II), 1M-$HClO_4$, 50% CH_3OH, reaction duration 10 min at 283 K. The excess of the Cr(II) ions was sufficient for the last complex of the series to be created in the reaction. The formed brown-red Cr(III) complex was eluted from the ion exchanger by solution of 0·01M-$HClO_4$ and 0·99M-$NaClO_4$ at 274 K. Its absorption spectrum agreed well with the published data[8]. The yields of the Cr(III) primary products are given in Table I. Obviously, approximately a half of the reacted Cr(II) ions convert to CrX^{2+} complexes. If the ratio $[CHX_3]_0/[Cr(II)]_0 \geqq 1$, hexaquochromic ions are formed only *via* aquation reactions of CrX^{2+} or of organochromic complexes. However, other reactions in which Cr^{3+} ions are produced may take place if the reaction system involves an amount of Cr(II) ions sufficient for additional reactions steps to occur.

Kinetics of formation of methane. Methane was found to form during reactions of Cr(II) with CHX_3 only after an induction period necessary for the occurrence of preceding reactions, even if the system was stirred vigorously (Fig. 3). It can be assumed that in the time corresponding to the maximum on the upper curve, the rate of formation becomes equal to the rate of decomposition of the methylchromic

TABLE I

Yields of Primary Cr(III) Products in the Oxidation–Reduction Reactions of Cr(II) with CHX_3 Medium of 1M-$HClO_4$, 50% CH_3OH.

X	Content in the reaction mixture mol		Yield of the complexes formed, %		
	Cr^{2+}	CHX_3	CrX^{2+}	organochromic	Cr^{3+}
Br	$1{\cdot}8 \cdot 10^{-4}$	10^{-4}	50	26	24
Br	$3{\cdot}6 \cdot 10^{-4}$	10^{-4}	42	31	27
Br	10^{-4}	$4 \cdot 10^{-4}$	51	49	0
Cl	$2 \cdot 10^{-4}$	$6 \cdot 10^{-3}$	50	18·5	31·5
Cl	$4 \cdot 10^{-4}$	$6 \cdot 10^{-3}$	51	30	19
I	10^{-4}	10^{-4}	46	54	0

complex. The time from which the concentration of Cr(II) ions no more decreases in the reaction with $CHBr_3$ was found by parallel polarographic monitoring of the Cr(II) ions concentration and volumetric monitoring of CH_4. After that time methane is formed according to 1st order kinetic equation. In agreement with the published kinetic equation for aquation of methylchromic complex[9], perchloric acid was found to accelerate the formation of methane. Our value of the 1st order rate constant for the methane formation, $k_{CH_4}^{295} = 1{\cdot}18 \,.\, 10^{-3}\,s^{-1}$ in 1M-$HClO_4$ and 42% CH_3OH, agrees better with the value $k_{CH_4} = 1{\cdot}33 \,.\, 10^{-3}\,s^{-1}$ in DMF–H_2O system[3] than with the rate constant of $CrCH_3^{2+}$ aquation, $k^{298} = 5{\cdot}2 \,.\, 10^{-3}\,s^{-1}$, in 1M-$HClO_4$ (ref.[9]).

DISCUSSION

The kinetic study of reactions of chloroform or bromoform with Cr(II) ions revealed that the activatied complex occurring during those reactions consists of one Cr(II) ion and one CHX_3 molecule. The formation of CrX^{2+} (X = Cl, Br, I) as the primary products requires a direct attack of the Cr(II) ion on the halogen of the haloform, *i.e.* a bridge activated complex of the composition $[(H_2O)_5CrXCHX_2^{2+}]^{\neq}$. The rate-controlling step is thus the reaction

$$\mathrm{Cr^{2+} + XCHX_2 \xrightarrow{k_1} CrX^{2+} + \dot{C}HX_2}\,, \qquad (B)$$

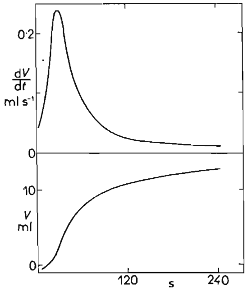

FIG. 3

Formation of Methane in the Reaction of Cr(II) with Bromoform

4·8 . 10^{-2}M-$CHBr_3$, 4·8 . 10^{-1}M-Cr(II), 0·05M-$HClO_4$, 48% CH_3OH, 295 K.

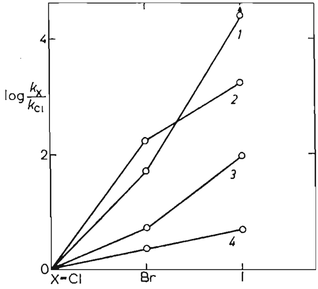

FIG. 4

Effect of the Halogen on the Reactivity of Cr(II) Ions with the Oxidants

[a] Ref.[10], [b] ref.[11], [c] this work. 1 CHX_3[c], 2 XCH_2COOH[b], 3 $[Cr(NH_3)_5X]^{2+}$[a], 4 $[Co(NH_3)_5X]^{2+}$[a].

and therefore change in the perchloric acid concentration or in the ionic strength has no effect on the rate. A fast reaction of the radical formed with another Cr(II) ion gives rise to $[CrCHX_2]^{2+}$, the first complex in the series of the organochromic complexes formed. As the kinetic measurements were conducted using a high excess of the oxidants, only those two reactions occurred, and therefore the rate constant in the rate equation (*1*) is $k = 2k_1$.

The electrostatic model of interaction in solution solely is not capable of accounting for the observed dependence of the rate constant of the oxidation–reduction reaction of Cr(II) ions with $CHBr_3$ on the mole fraction of the nonaqueous solvent. The medium affects the composition of the coordination sphere of the extremely substitution-unstable Cr(II) complexes, and thus part of the water molecules can be replace- by molecules of the co-solvent. Probably, a composition of the coordination sphere exists that is most favourable for electron transfer within the binuclear unit. The negative effect of acetic acid on the reactivity may reflect its poorer solvation ability.

The stoichiometry of the oxidation–reduction reactions and the nature of the products imply the occurrence of consecutive steps, in which Cr(II) ions are consumed and additional organochromic complexes are formed. In the case of bromo- and dibromomethylchromic complexes, direct reaction with Cr(II) ions, analogous to those observed for dichloro- and iodomethylchromic complexes[5-7], are also assumed. The production of methane in all the three systems studied can be explained in terms of acidolysis of the methylchromic complex according to the equation

$$[(H_2O)_5CrCH_3]^{2+} + H_3O^+ \rightarrow [Cr(H_2O)_6]^{3+} + CH_4\,. \qquad (C)$$

In the oxidation-reduction reaction of Cr(II) ions with $CHBr_3$, the reaction orders with respect to the reactants are the same in the two systems used. The formation of halochromic complexes also indicates that the bridging Cr–X–C structure remains preserved in both systems. The presence of acetic acid manifests itself particularly in the subsequent stages, as the decomposition of halomethylchromic complexes was found to be faster in the acetic acid system than in the methanolic system, with partial formation of acetatochromic complexes.

Based on the experimental results obtained, it is possible to postulate the inner-sphere mechanism of electron transfer between Cr(II) ions and haloforms and to evaluate the relative efficiency of the bridging halogens. The order of reactivities in these reactions is $k_I > k_{Br} > k_{Cl}$, which is the normal sequence. However, the observed rate constants are products of the equilibrium constants of formation of the precursor and the rate constants of the electron transfer within the binuclear complexes themselves. Common considerations concerning the stability constants of Cr(II) complexes with halide ions suggest, however, that the thermodynamic contributions in the observed rate constants should exhibit an opposite trend, inasmuch as the strength of the bridge formed grows in the order I < Br < Cl. Also, in the series in question, the stability of the Cr(III) products is highest for the chlorochromic complex.

As can be seen from Fig. 4, replacement of the bridge ligand in the reaction of the complex compounds concerned has a smaller effect on the rate of the oxidation-reduction reaction with Cr(II) ions than in the case of the Cr–X–C bridge structure. At the same time this indicates that the nature of the central atom of the oxidant affects appreciably the rate of the electron transfer *via* the same bridge in the resonance type inner-sphere mechanism. In compounds involving a C–X bond the polarity and the bond strength decrease in the order Cl > Br > I and the polarizability decreases in the reverse order, which in the case of activation cleavage of this bond favours the normal order as observed. Since in the oxidation–reduction reaction under study the C–X bond does undergo cleavage, the energy of the bond can be expected to have a bearing on the value of the rate constant.

The activation Gibbs energy of the oxidation–reduction reactions studied increases with the dissociation energy of the C–X bond in the haloforms[12]. This indicates that the effect of the C–X bond cleavage in the oxidation–reduction reactions of Cr(II) with CHX_3 is of greater importance than the effect of the Cr–X bond formation and controls the rate of the halogen atom transfer from the haloform to Cr(II).

REFERENCES

1. Taube H.: Ber. Bunsenges. Phys. Chem. *76*, 964 (1972).
2. Anet F. A. L.: Can. J. Chem. *37*, 58 (1958).
3. Castro C. E., Kray W. C. jr: J. Amer. Chcem. Soc. *88*, 4447 (1966).
4. Dodd D., Johnson M. D.: J. Chem. Soc. A *1968*, 34.
5. Nohr R. S., Spreer L. O.: Inorg. Chem. *13*, 1239 (1974).
6. Nohr R. S., Spreer L. O.: J. Amer. Chem. Soc. *96*, 2618 (1974).
7. Espenson J. H., Leslie J. P. II.: Inorg. Chem. *15*, 1886 (1976).
8. Espenson J. H., Williams D. A.: J. Amer. Chem. Soc. *96*, 1008 (1974).
9. Schmidt W., Swinehart J. H., Taube H.: J. Amer. Chem. Soc. *93*, 1117 (1971).
10. Taube H.: *Electron Transfer Reactions of Complex Ions in Solution*, p. 51. Academic Press, New York 1970.
11. Ševčík P., Jakubcová D.: This Journal *42*, 1767 (1977).
12. Miller W. J., Palmer H. B.: J. Chem. Phys. *40*, 3701 (1964).

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