

## THE KINETICS AND MECHANISM OF OXIDATION OF Cr(II) IONS BY DICHLOROACETIC ACID

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The kinetics and mechanism of oxidation of Cr(II) ions by dichloroacetic acid in aqueous HClO<sub>4</sub> solution was studied. The reaction proceeds under the consumption of 2 mol of Cr<sup>2+</sup> per 1 mol of Cl<sub>2</sub>HCCOOH to give 1 mol of CrCl<sub>2</sub><sup>+</sup>. The redox reaction is first order in both reactants. The rate constant (at 25°C),  $k_1$ , for the reaction path involving the dichloroacetate ion has a value of 0.11 mol<sup>-1</sup> s<sup>-1</sup> ( $\Delta H^\ddagger = 9.2$  kcal mol<sup>-1</sup>,  $\Delta S^\ddagger = -32.3$  e.u.) and the constant  $k_2$  for the reaction of undissociated dichloroacetic acid with Cr(II) ions equals to 0.251 mol<sup>-1</sup> s<sup>-1</sup> ( $\Delta H^\ddagger = 9.2$  kcal mol<sup>-1</sup>,  $\Delta S^\ddagger = -31.1$  e.u.). The organochromium complex (H<sub>2</sub>O)<sub>5</sub>CrCl(Cl)(H).COOH<sup>2+</sup> is formed during the redox reaction. The rate of its aquation ( $k_{\text{obs}} = 1.66 \cdot 10^{-5}$  s<sup>-1</sup> at 25°C,  $\Delta H^\ddagger = 24.5$  kcal mol<sup>-1</sup>,  $\Delta S^\ddagger = 1.5$  e.u.) in 1M-HClO<sub>4</sub> places the complex to a class of substitution-stable Cr(III) complexes. Acetic acid, dichloroacetic acid and Cr(II) ions accelerate its decomposition. The reaction mechanism of the redox reaction is proposed in which the rate-determining step is assumed to be transfer of chlorine atom from dichloroacetic acid to Cr<sup>2+</sup> via a bridge activated complex of the structure [(H<sub>2</sub>O)<sub>5</sub>CrCl(Cl)(H)COOH<sup>2+</sup>]<sup>‡</sup>.

The study of reduction of carboxylato-pentaamminecobalt(III) complexes with Cr(II) ions has played the most important role during the development of ideas about mechanism of redox reactions in which electron transfer is realized through an organic bridge group<sup>1,2</sup>. From this standpoint, a study of reduction of free carboxylic acids is both interesting and useful. A preliminary investigation of redox reactions of Cr(II) ions with monochloroacetic and dichloroacetic acids<sup>3</sup> has been made with a view to examine the interfering effect of the above reactions on the kinetics of reduction of mono- and dichloroacetato-pentaamminecobalt(III) complexes by Cr(II) ions. The complex (H<sub>2</sub>O)<sub>5</sub>CrCH(Cl)COOH<sup>2+</sup>, a probable intermediate<sup>3</sup>, is assumed to be responsible for the exceptionally high absorbance at 415 nm observed in the reaction of Cr(II) ions with dichloroacetic acid. Transfer of chlorine from the oxidant to Cr(II) has been evidenced and formation of (H<sub>2</sub>O)<sub>5</sub>CrCCl<sub>2</sub>COOH<sup>2+</sup> has been indicated in the kinetic study of oxidation of Cr(II) ions with trichloroacetic acid<sup>4</sup>.

The present work was performed with the aim to propose mechanism of oxidation of Cr(II) ions with dichloroacetic acid on the basis of a detailed kinetic investigation of this reaction in aqueous HClO<sub>4</sub> solution as well as to study some spectral and kinetic properties of the presumed organochromium intermediate.

## EXPERIMENTAL

**Chemicals.** All stoichiometric and kinetic measurements were carried out in an atmosphere of nitrogen. The nitrogen (for lamps) was purified by passing through a solution of Cr(II) ions which was obtained from  $\text{KCr}(\text{SO}_4)_2$ ,  $\text{H}_2\text{SO}_4$ , and zinc amalgam. The solutions were prepared from analar grade chemicals and distilled water. Solutions of  $\text{Cr}(\text{ClO}_4)_2$  were prepared by dissolving excess metallic chromium (99.997%, Fluka A-G, Buchs) in perchloric acid (usually 0.1 to 1M) at 23–25°C for 10–14 h and were stored under nitrogen. Before dissolving, the chromium was necessary to activate in 6M-HCl. The amount of Cr(III) impurities in these solutions was determined polarographically, from the ratio of limiting diffusion anodic current of Cr(II) ions ( $E_{1/2} = -0.36$  vs N.C.E. in 1M-HClO<sub>4</sub>) to the height of cathodic wave of Cr(III) ions ( $E_{1/2} = -0.98$  V vs N.C.E. in 1M-HClO<sub>4</sub>). An average amount of Cr(III) impurities was 6–7% of the concentration of Cr(II) ions in these solutions. A total chromium concentration was determined spectrophotometrically (at 372 nm,  $\epsilon = 4830 \text{ l mol}^{-1} \text{ cm}^{-1}$ , *cf.*<sup>5</sup>) after oxidation to the chromate by an alkaline solution of hydrogen peroxide.

**Analyses.** Cr(III) complexes were separated from other reaction products by ion-exchange chromatography. The column (1 × 8 cm) filled with Dowex 50W-X2 (200–400 mesh) was washed with 3M-HClO<sub>4</sub> (100 ml) and then by distilled water until pH reached a value of 5.5. This procedure ensured that the column was exclusively in the H<sup>+</sup> form. Then 10<sup>-4</sup> to 10<sup>-3</sup> moles of Cr(III) were introduced from the reaction mixture, the ionic strength of which was adjusted by distilled water to a value of below 0.1 mol l<sup>-1</sup>. Cr(III) complexes with the +2 charge were eluted usually with 0.5M-HClO<sub>4</sub>. The product of oxidation of Cr(II) by air oxygen,  $\text{Cr}_2(\text{OH})_2^{4+}$ , was removed from the column by 4M-HClO<sub>4</sub>. The elution time varied from 20 to 70 min, ensuring that the results were not affected by consecutive reactions of  $\text{CrX}^{2+}$  complexes. After separation on the ion-exchange column, Cr(III) complexes were identified spectrophotometrically with Specord UV VIS instrument (Zeiss, Jena, GDR).  $(\text{H}_2\text{O})_5\text{CrOOCCH}_2\text{Cl}^{2+}$  and  $(\text{H}_2\text{O})_5\text{Cr}(\text{OOCCHCl}_2)^{2+}$  were used as standards for the complexes with the +2 charge. These were prepared by substitution reactions of 1M-Cr(H<sub>2</sub>O)<sub>6</sub><sup>3+</sup> with 1M solutions of mono- and dichloroacetic acid, respectively, in 0.5M-HClO<sub>4</sub> at 23°C till the equilibrium was achieved. The complexes were separated from standard Cr<sup>3+</sup> solution (Serba International) by means of an ion exchanger. Dichloroacetic acid (analar grade, Ferak, Berlin, GDR) was purified before use by distillation under reduced pressure (10 Torr, 95°C) and its purity was verified by gas-liquid chromatography. Chloride ions which were one of the final reaction products were determined by potentiometric titration with silver nitrate solution. The pH-meter used (Model OP 204/1 Radelkis, Hungary) was equipped with silver and calomel electrode as indicative and reference electrode, respectively.

Organic products were identified by gas-liquid chromatography from the ether extracts of final reaction products. The reaction mixture consisted of 40 ml of 0.5M-Cr(II), 2.5 ml of Cl<sub>2</sub>HCCOOH, and 2.76 ml of HClO<sub>4</sub>. The redox reaction was practically complete at 21°C after 5 min. Primary products were subjected to aqutation for 8 h at 75°C and then they were extracted five times with 20–30 ml portions of diethyl ether. The extract was condensed by evaporating the solvent to a volume of 2 ml, made alkaline with 5% NaOH solution (pH 10), and the mixture was evaporated to dryness *in vacuo*. Then 2 ml of dry methanol were added to the residue and the mixture was adjusted by conc. sulphuric acid to pH 1, refluxed for 1/2 h, and then introduced into the column filled with dry silica gel topped with a layer of anhydrous sodium sulphate. The elution was made with a small amount of methanol and the eluate was directly fed to the chromatograph Fractovap 2407 T, Carlo Erba) equipped with a flame-ionization detector and a 2 m-column (3 mm i.d.) packed with 10% PEG 400 on Chromosorb W (60–80 mesh) (80 and 90°C oven temperature, 140°C injection port temperature, nitrogen as a carrier gas, 0.1–0.2 µl-samples).

Individual components of reaction mixtures were identified by comparing their elution data with those of authentic samples of acetic, monochloro- and dichloroacetic acids.

**Kinetics.** Kinetics of redox reaction of Cr(II) ions with dichloroacetic acid in aqueous  $\text{HClO}_4$  was examined polarographically. The time dependence of the limit diffusion current of Cr(II) ions at a constant potential of 0 V vs N.C.E. was recorded. A sufficient excess of the oxidant (at least tenfold) allowed to calculate rate constants  $k_{\text{obs}}$  from the pseudo-first order equation (1) where  $I_0$  is the limit diffusion current of Cr(II) ions in the beginning of the reaction and  $I$  is the current in time  $t$ . Stoichiometry of the redox reaction was determined by polarometric titration, utilizing polarographic activity of both Cr(II) and Cr(III) complexes. The kinetic procedure and experimental arrangement used were described in detail in previous works<sup>4,6</sup>.

Kinetics of reactions of Cr(III) primary products was examined spectrophotometrically at 280 and 410 nm, *i.e.* at the absorption maxima of the organochromium(III) complex. Rate constants  $k'_{\text{obs}}$  were calculated from Eq. (2), where  $A_0$  is the absorbance at the beginning of the reaction,  $A_\infty$  is the absorbance at the end of the reaction, and  $A$  is the absorbance in time  $t$ .

$$\log(I_0/I) = (k_{\text{obs}}/2.303) t, \quad (1)$$

$$\log(A_0 - A_\infty)/(A - A_\infty) = (k'_{\text{obs}}/2.303) t. \quad (2)$$

## RESULTS

### *Stoichiometry of Redox Reaction of Cr(II) Ions with Dichloroacetic Acid*

The stoichiometry was determined by polarometric titrations of *a*) Cr(II) ions with dichloroacetic acid and *b*) dichloroacetic acid by Cr(II) ions in 0.01–0.8M- $\text{HClO}_4$  (Fig. 1). The limit diffusion current of Cr(II) and Cr(III) ions was measured at 0 V and  $-1.2$  V vs N.C.E., respectively. The  $E_{1/2}$  value of dichloroacetic acid is  $-1.65$  V against N.C.E. in 1M- $\text{NaClO}_4$ . In the medium of perchloric acid its wave is

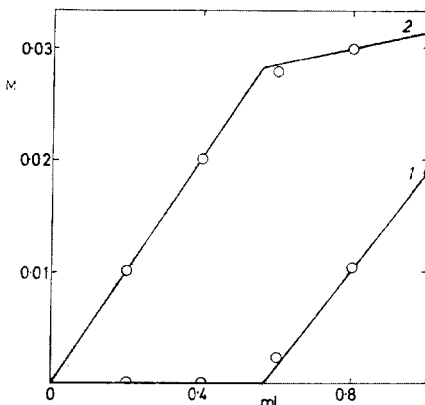


FIG. 1  
Polarometric Titration of 10 ml of 0.0125M- $\text{Cl}_2\text{CHCOOH}$  by 0.442M-Cr(II)  
0.01M- $\text{HClO}_4$ , 25°C, Ionic Strength 0.8:  
1 [Cr(II)], 2 [Cr(III)].

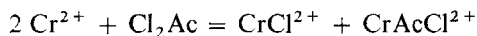
suppressed by evolution of hydrogen and does not interfere with the waves of Cr(III) and Cr(II). The interval between two additions of the titrating agent was 30 min, which represents 6–7 half-times of the reaction. Methods *a*) and *b*) showed that 2 mol of Cr(II) are consumed per 1 mol of dichloroacetic acid. It was confirmed by gas chromatographic analysis that methyl ester of monochloroacetic acid is the final reaction product; traces of acetic acid found were present also in standards.

Chromatographic separation of Cr(III) complexes on Dowex 50W–X<sub>2</sub> indicated formation of the two (green and violet) bands of approximately equal width which were completely eluated and distinctly separated by 0.5–0.8M-HClO<sub>4</sub>. This observation excludes the possibility that Cr<sub>2</sub>(OH)<sub>2</sub><sup>4+</sup> are formed as products of the redox reaction studied. The green band was eluated at a faster rate (it passed through the column in 40–50 min) then the violet band (the time of its complete elution equaled to 60–70 min). On using 0.1M-HClO<sub>4</sub> as an eluent, Cr(III) complexes remained at the start of the column even after elution had been made for several hours. Both bands were eluated faster than the standard solution of Cr(H<sub>2</sub>O)<sub>6</sub><sup>3+</sup>. These findings led to conclusion that the complexes bear the +2 charge. The absorption spectrum of the green complex shows maxima at 430 nm ( $\epsilon = 20.8 \text{ l mol}^{-1} \text{ cm}^{-1}$ ) and 610 nm ( $\epsilon = 16.5 \text{ l mol}^{-1} \text{ cm}^{-1}$ ). The position and relative height of these absorption maxima correspond to the complex (H<sub>2</sub>O)<sub>5</sub>CrCl<sup>2+</sup> (ref.<sup>7</sup>). The position of absorption maxima and the values of absorption coefficients of the violet band depended upon reaction conditions, which indicated that we deal here with a mixture of Cr(III) complexes. Repeated separation showed that the second band consists of two fractions; a red one that is eluated at a faster rate than a blue-violet fraction. Both fractions always overlapped in the centre. Multiple separation connected with collection of the first (last) fraction made it possible to obtain both relatively pure components of the second band. The red Cr(III) complex shows absorption maxima at 280 nm ( $\epsilon = 4620 \text{ l mol}^{-1} \text{ cm}^{-1}$ ), 414 nm ( $\epsilon = 114 \text{ l mol}^{-1} \text{ cm}^{-1}$ ), and 540 nm ( $\epsilon = 50 \text{ l mol}^{-1} \text{ cm}^{-1}$ ). The blue-violet band has maxima at 414 nm ( $\epsilon = 23.5 \text{ l mol}^{-1} \text{ cm}^{-1}$ ) and 579 nm ( $\epsilon = 22.5 \text{ l mol}^{-1} \text{ cm}^{-1}$ ). Similar values were determined also for the standards, (H<sub>2</sub>O)<sub>5</sub>CrOOCCH<sub>2</sub>Cl<sup>2+</sup> ( $\epsilon_{414} = 23.2$  and  $\epsilon_{580} = 22.3$ ) and (H<sub>2</sub>O)<sub>5</sub>.CrOOCCHCl<sub>2</sub><sup>2+</sup> ( $\epsilon_{414} = 24.5$  and  $\epsilon_{582} = 24$ ). For the sake of simplicity, a mixture of the red and violet-blue complex, *i.e.* the second band, will be further denoted as CrAcCl<sup>2+</sup>. CrCl<sup>2+</sup> and CrAcCl<sup>2+</sup> undergo slowly aquation to the hexaaquo-chromium(III) complex. After 15 h in 0.8M-HClO<sub>4</sub> at 70°C, the spectrum of both complexes ( $\epsilon_{410} = 16.5$  and  $\epsilon_{578} = 13.6$ ) resembles the spectrum of Cr(H<sub>2</sub>O)<sub>6</sub><sup>3+</sup> ions.

Attention has also been paid to quantitative analysis of the Cr(III) complex formed. The redox reaction was allowed to proceed under different reaction conditions. After separation on an ion-exchanger, their concentration in individual bands was determined and the number of mol of CrCl<sup>2+</sup> and CrAcCl<sup>2+</sup> formed per 1 mol of Cr(II) consumed was calculated, allowing for the contamination of Cr(II) reactant solutions by Cr(III) ions. The results are summarized in Table I. The results show

that under all the conditions chosen, 1 mol of Cr(II) produces always 0.5 mol of  $\text{CrCl}^{2+}$  and 0.5 mol of  $\text{CrAcCl}^{2+}$ . This ratio is not affected by the presence of either chloride or bromide ions.

From this it follows that the redox stoichiometry can be exactly expressed by the equation



and the overall stoichiometric equation of the oxidation of Cr(II) ions by dichloroacetic acid is

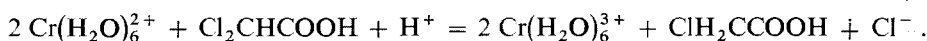


TABLE I

Distribution of Cr(III) Primary Products

$[\text{HClO}_4]$	$[\text{Cr}^{2+}]_0$	$[\text{Cl}_2\text{HC COOH}]_0$	$R_1^a$	$R_2^b$
0.2	0.0420	0.04	0.48	0.45
0.2	0.0410	0.08	0.49	0.49
0.01	0.0410	0.08	0.46	0.49
0.05	0.0190	0.2	0.48	0.49
0.1 <sup>c</sup>	0.0193	0.2	0.49	0.49
0.1 <sup>d</sup>	0.0193	0.2	0.48	0.48

<sup>a</sup> The number of mol of  $\text{CrCl}^{2+}$  formed from 1 mol of  $\text{Cr}^{2+}$ . <sup>b</sup> The number of mol of  $\text{CrAcCl}^{2+}$  formed from 1 mol of  $\text{Cr}^{2+}$ . <sup>c</sup>  $[\text{Cl}^-] = 0.7\text{M}$ . <sup>d</sup>  $[\text{Br}^-] = 0.7\text{M}$ .

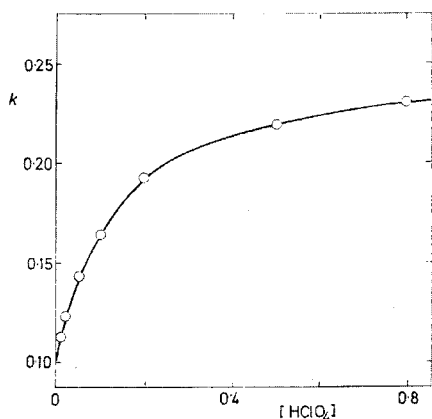


FIG. 2  
Plot of Rate Constant  $k$  ( $\text{l mol}^{-1} \text{s}^{-1}$ )  
against  $[\text{HClO}_4]$   
25°C, ionic strength 0.8.

*Kinetics of Redox Reaction*

Kinetics of the oxidation of Cr(II) ions by dichloroacetic acid was examined using  $[\text{Cr(II)}]_0 \leq 2 \cdot 10^{-3}\text{M}$ ,  $[\text{Cl}_2\text{Ac}]_0 = 1-5 \cdot 10^{-2}\text{M}$ ,  $[\text{HClO}_4]_0 = 0.01-0.8\text{M}$ ,  $[\text{Cl}^-]$  or  $[\text{Br}^-] = 0-0.7\text{M}$ , ionic strength of 0.1-1.5, and a temperature of 17-45°C. On using dichloroacetic acid in sufficient excess, the reaction obeyed the first-order equation (1) at least to 90% conversion. The dependence  $k_{\text{obs}} = f([\text{Cl}_2\text{Ac}])$  is linear and passes through the origin, which proves that the reaction is first order also in dichloroacetic acid. The rate constant  $k$  determined from the slope of this dependence obtained for 0.5M-HClO<sub>4</sub>, ionic strength 0.5, and 25°C has a value of  $0.19 \pm 0.01 \text{ l mol}^{-1}\text{s}^{-1}$ . The rate law of the oxidation of Cr(II) ions by dichloroacetic acid has the following form:

$$-d[\text{Cr(II)}]/dt = k[\text{Cr(II)}][\text{dichloroacetic acid}].$$

The rate constant  $k$  depends on concentration of perchloric acid (Fig. 2). Considering dissociation of dichloroacetic acid and parallel reduction of both forms, the rate constant of the oxidation can be expressed in the form (3), where  $k_1$  is the constant of reduction of dissociated dichloroacetic acid,  $k_2$  is the rate constant of the reaction of the undissociated acid and  $K$  is reciprocal value of the dissociation constant ( $K_D^{25} = 5.1 \cdot 10^{-2} \text{ mol l}^{-1}$ ). Eq. (3) agrees well with experimental results.

$$k = (k_1 + k_2K[\text{H}^+])/(1 + K[\text{H}^+]). \quad (3)$$

The rate constants  $k_1$  and  $k_2$  determined from this equation are presented in Table II. The values of activation parameters were obtained from the Eyring equation:  $\Delta H^\ddagger = 9.2 \pm 0.6 \text{ kcal mol}^{-1}$  and  $\Delta S^\ddagger = -32.3 \pm 2 \text{ e.u.}$  for reaction of the dissociated acid,  $\Delta H^\ddagger = 9.2 \pm 0.6 \text{ kcal mol}^{-1}$  and  $\Delta S^\ddagger = -31.1 \pm 2 \text{ e.u.}$  for reaction of the undissociated acid.

The effect of ionic strength (adjusted by NaClO<sub>4</sub>) upon rate constant depended on the concentration of HClO<sub>4</sub>. In 0.1M-HClO<sub>4</sub> the rate constant  $k$  slowly decreases with increasing ionic strength from 0.1 to 0.4 (by 7%), at ionic strength 0.4 there was a flat minimum, and at a 0.4 to 1.5 region the rate constant slowly increases (by 20%). In 0.4M-HClO<sub>4</sub> the rate constant increased with increasing ionic strength (0.4-1.5) (at maximum by 30%). Chloride and bromide ions (0-0.7M) in 0.1M-HClO<sub>4</sub> did not essentially affect the rate constant of oxidation of Cr(II) ions by dichloroacetic acid.

As to kinetics of decomposition of the organochromium(III) complex, it was found by following the temperature dependence of the rate constant of aequation (Eq. (2)) of  $(\text{H}_2\text{O})_5\text{CrCH}(\text{Cl})\text{COOH}^{2+}$  in 1M-HClO<sub>4</sub> that activation parameters have the following values:  $\Delta H^\ddagger = 24.5 \pm 0.8 \text{ kcal mol}^{-1}$  and  $\Delta S^\ddagger = 1.5 \pm 3 \text{ e.u.}$  Moderate

increase in the rate constant (by 25%) was found for 0.01M-HClO<sub>4</sub>. Effects of HClO<sub>4</sub>, Cr(II), and Cl<sub>2</sub>HCCOOH on the kinetics of decomposition of the organochromium(III) complex are graphically represented in Fig. 3. These results allowed to estimate the effect of reactants and reaction time on the yields of (H<sub>2</sub>O)<sub>5</sub>CrCH(Cl).COOH<sup>2+</sup> in the redox reaction (Table III).

## DISCUSSION

The activated complex for oxidation of Cr(II) ions by dichloroacetic acid contains 1 mol of Cr(II) and 1 mol of the oxidizing agent. As follows from the stoichiometry of the redox reaction, which requires 2 mol of Cr(II) per 1 mol of Cl<sub>2</sub>HCCOOH, the oxidizing agent is a two-electron reactant. As the stoichiometry of the redox reaction differs from that of the activation step, unstable oxidation states of one of the two reactants must be considered in the mechanism of the reaction. In systems in which

TABLE II  
Temperature Dependence of Rate Constants  $k_1$  and  $k_2$  (l mol<sup>-1</sup> s<sup>-1</sup>)

°C	$k_1$	$k_2$	°C	$k_1$	$k_2$
17.0	0.06	0.13	35.0	0.17	0.35
25.0	0.10	0.25	45.0	0.30	0.57

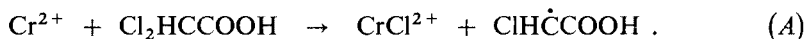
TABLE III  
Effects of Reactants and Reaction Time on Yields of (H<sub>2</sub>O)<sub>5</sub>CrCH(Cl)COOH<sup>2+</sup>(A)

[Cl <sub>2</sub> CHCOOH] <sub>0</sub>	[Cr <sup>2+</sup> ] <sub>0</sub>	<i>t</i> , min	A <sup>a</sup>	
			uncorr.	corr. <sup>b</sup>
0.2	0.04	3	34.2	36.5
0.2	0.04	30	21.7	38.0
0.005	0.01	30	39.0	40.0

<sup>a</sup> The amount of the organochromium(III) complex in per cent of the total amount of Cr(III) in CrAcCl<sup>2+</sup>. <sup>b</sup> After allowance had been made for the effect of reactants and reaction time; 0.5M-HClO<sub>4</sub>, 21°C.

the presence of Cr(IV) is proposed, binuclear complexes  $\text{Cr}_2(\text{OH})_2^{4+}$  are formed<sup>8,9</sup> that undergo slow decomposition and can be easily identified. These binuclear complexes do not arise in the redox reaction of Cr(II) ions with dichloroacetic acid. It seems thus reasonable to assume that the reaction involves two consecutive one-electron steps.

The reaction mechanism that comports with experimental results involves transfer of chlorine atom from dichloroacetic acid to Cr(II) in the rate-determining step (Equation (A)) via activated bridge complex,  $[(\text{H}_2\text{O})_5\text{CrClCH}(\text{Cl})\text{COOH}^{2+}]^\ddagger$ .



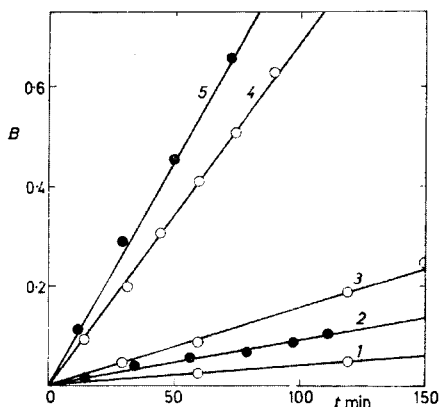
The presumption that the redox reaction proceeds by inner sphere mechanism is supported by the following facts: 1)  $(\text{H}_2\text{O})_5\text{CrCl}^{2+}$  is primary product instead of thermodynamically preferred combination  $\text{Cr}(\text{H}_2\text{O})_6^{3+} + \text{Cl}^-$ , and 2) 1 mol of  $(\text{H}_2\text{O})_5\text{CrCl}^{2+}$  is formed per 1 mol of the reduced dichloroacetic acid and this ratio does not depend on the ratio of initial concentrations of the reactants,  $[\text{H}^+]$ , or the presence of chloride ions in the reaction mixture. The fact that acetic acid is not reduced by Cr(II) ions while their chloro derivatives are throws light on the site of attack of Cr(II) on the oxidizing agent. This is in accordance with selective reduction of halogeno or nitro groups of organic compounds by Cr(II) salts while carbonyl groups of these compounds remain unaffected<sup>10</sup>. The reaction (A) is analogous to reductions of some alkyl halogenides<sup>11</sup> and trichloroacetic acid<sup>4</sup> by Cr(II) ions in which halogeno-pentaaquochromium(III) ions and organic radicals are formed in the first, one-electron, inner-sphere step.

FIG. 3

Effects of  $\text{HClO}_4$ ,  $\text{Cl}_2\text{HCCOOH}$ , and Cr(II) Ions upon Pseudo-First Order Decomposition of the Organochromium(III) Complex

$$\left( B = \log \frac{A_0 - A_\infty}{A - A_\infty} \right)$$

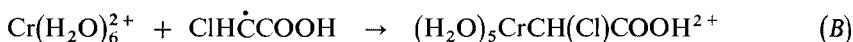
1 1M- $\text{HClO}_4$ , 25°C, 2 0.5M- $\text{HClO}_4$ , 0.01M- $\text{Cl}_2\text{HCCOOH}$ , 25°C, 3 0.8M- $\text{HClO}_4$ ,  $3.7 \cdot 10^{-3}$ M-Cr(II), 25°C, 4 0.8M- $\text{HClO}_4$ , 0.1M-Cr(II), 21.8°C, 5 0.5M- $\text{HClO}_4$ , 0.2M- $\text{Cl}_2\text{HCCOOH}$ , 21.8°C.





The form of the rate law for the reduction of trichloroacetic acid by Cr(II) ions<sup>4</sup> excluded to distinguish kinetically between trichloroacetate ion and the acid. With regard to the rate-determining transfer of chlorine atom to Cr(II), it can be expected that electrostatic effect of relatively remote carboxylic group on this transfer would not be important. For that reason, similarity in the values of  $k_1$  and  $k_2$  is not surprising. The agreement with earlier reported data is satisfactory. The contribution of the reaction path inversely dependent on hydrogen ion concentration for the reduction of dichloroacetic acid by Cr(II) ions was expressed by Taube<sup>3</sup> by  $k_1 = 0.07 \pm \pm 0.03 \text{ l mol}^{-1} \text{ s}^{-1}$  and of the reaction path independent of  $[\text{H}^+]$  by  $k_2 = 0.15 \pm \pm 0.06 \text{ l mol}^{-1} \text{ s}^{-1}$  (for 25°C, unspecified ionic strength).

A  $\text{ClH}\ddot{\text{C}}\text{COOH}$  radical that is produced in the rate-determining step can react readily with another Cr(II) ion. This reaction leads to formation of an organochromium(III) cation (Eq. (B)). The absorption spectrum of the second (violet) band



separated on an ion exchanger shows, however, that formation of the organochromium(III) complex is not quantitative. The position and intensity of absorption bands of the red fraction of the second band clearly points to formation of a Cr(III) complex with the Cr—C bond<sup>11-13</sup>. The Cr(III) complexes with Cr—O bond that were prepared by substitution reaction of  $\text{Cr}^{3+}$  with mono- or dichloroacetic acid had absorption spectra similar to the spectrum of the purified, second (blue-violet) fraction of the second band. The shape of the spectrum of the second band as a whole depended upon initial concentrations of the reactants and upon reaction time. The values of  $\epsilon_{412}$  ( $\sim 40 \text{ l mol}^{-1} \text{ cm}^{-1}$ ) and  $\epsilon_{582}$  ( $\sim 30 \text{ l mol}^{-1} \text{ cm}^{-1}$ ) were obtained for twofold to tenfold excess of dichloroacetic acid and reaction time of 30 min at 25°C. This indicates that the second band may involve a mixture of  $(\text{H}_2\text{O})_5\text{CrCH}(\text{Cl}) \cdot \text{COOH}^{2+}$ ,  $(\text{H}_2\text{O})_5\text{CrOOCCH}_2\text{Cl}^{2+}$ , and  $(\text{H}_2\text{O})_5\text{CrOOCCHCl}_2^{2+}$  that is formed by the reactions discussed later.

Acetic acid is an efficient catalyst for solvolysis of organochromium(III) complexes<sup>11,14</sup>. A solution of 1M- $\text{CH}_3\text{COOH}$  induces a practically complete decomposition of alkyl(ene)chromium(III) complexes in 5 min and the acid is thus much more effective than  $\text{H}_2\text{SO}_4$ ,  $\text{HClO}_4$  or  $\text{HCl}$  (of the same concentration)<sup>11</sup>. A similar influence of acetic acid was also observed in decomposition of  $(\text{H}_2\text{O})_5\text{CrCH}(\text{Cl}) \cdot \text{COOH}^{2+}$  formed in the redox reaction under study. In contrast to this, substitution inertness of this complex in 1M- $\text{HClO}_4$  is documented by  $k'_{\text{obs}} = 1.66 \cdot 10^{-5} \text{ s}^{-1}$  for aquation rate at 25°C and by  $\Delta H^\ddagger = 24.5 \text{ kcal mol}^{-1}$  and  $\Delta S^\ddagger = 1.5 \text{ e.u.}$  These values correspond to typical substitution reactions of inert Cr(III) complexes<sup>15</sup>.

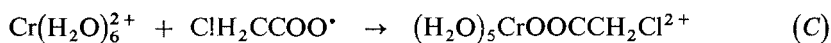
Catalytic effect of acetic acid has led us to study substitution stability of  $(\text{H}_2\text{O})_5 \cdot \text{CrCH}(\text{Cl})\text{COOH}^{2+}$  in dichloroacetic acid that was used in excess in the redox reaction. The values of  $k'_{\text{obs}} = 3.51 \cdot 10^{-5} \text{ s}^{-1}$  at 25°C and  $3.45 \cdot 10^{-4} \text{ s}^{-1}$  at 22°C,

for decomposition rate of  $(\text{H}_2\text{O})_5\text{CrCH}(\text{Cl})\text{COOH}^{2+}$  in 0.5M- $\text{HClO}_4$  and 0.01M- and 0.2M- $\text{Cl}_2\text{HCCOOH}$  demonstrate catalytic action of dichloroacetic acid. Decomposition of the organochromium(III) cation in this medium, similarly as in acetic acid, does not lead to hexaquo chromium(III) ions but to Cr(III) complexes with dichloroacetic acid or acetic acid containing Cr—O bond and having  $\epsilon_{414} \sim 26 \text{ l mol}^{-1}\text{cm}^{-1}$  and  $\epsilon_{580} \sim 24 \text{ l mol}^{-1}\text{cm}^{-1}$ .

From kinetic effect of dichloroacetic acid it was possible to estimate the amount of  $(\text{H}_2\text{O})_5\text{CrCH}(\text{Cl})\text{COOH}^{2+}$  that was decomposed by the action of the acid during the redox reaction. It was found that 40% of the organochromium(III) ions formed decompose during 30 min of the redox reaction in 0.2M- $\text{Cl}_2\text{HCCOOH}$  at 22°C.

Catalytic effect of Cr(II) ions on decomposition of the above organochromium(III) complex was observed earlier<sup>3</sup>. Our study shows that this complex cannot be isolated from the column of ion exchanger when the redox reaction is carried out with approx. 20fold excess of Cr(II). The effect of Cr(II) ions on its decomposition in 0.8M- $\text{HClO}_4$  at 25°C is demonstrated by  $k'_{\text{obs}} = 6.3 \cdot 10^{-5}\text{s}^{-1}$  in the presence of  $3.7 \cdot 10^{-3}\text{M}$ -Cr(II) and by  $k'_{\text{obs}} = 2.7 \cdot 10^{-4}\text{s}^{-1}$  in 0.5M- $\text{HClO}_4$  at 22°C and in the presence of 0.1M-Cr(II). With regard to the fact that in the redox reaction proper the  $[\text{Cr(II)}]_0$  to  $[\text{Cl}_2\text{HC} \cdot \text{COOH}]_0$  ratio was approx. 1/10 and in analysis of Cr(III) product distribution it was 1/10 to 1, this effect did not play a role here.

From the above discussion it follows that the amount of the red complex,  $(\text{H}_2\text{O})_5 \cdot \text{CrCH}(\text{Cl})\text{COOH}^{2+}$ , isolated by means of the ion exchanger (in contrast to the green complex,  $(\text{H}_2\text{O})_5\text{CrCl}^{2+}$ ) depends upon initial concentration of Cr(II) and dichloroacetic acid (these reactants affect also the reaction time necessary to carry out reaction to 6–7 half times), upon temperature (substantially higher value of  $\Delta H^\ddagger$  of the substitution reaction compared to  $\Delta H^\ddagger$  of the redox reaction) and, to a lesser extent, also upon  $\text{H}^+$  concentration. The highest relative yields of the organochromium(III) complex were obtained on using stoichiometric concentrations of the reactants. After allowing for the effect of  $\text{HClO}_4$ ,  $\text{Cl}_2\text{HCCOOH}$  and Cr(II) ions, approximately equal yields of the organochromium(III) complex were obtained for the redox reaction. These corrected yields do not represent more than c. 40% of the total amount of Cr(III) complexes present in the second band. It seems therefore likely that another fast reaction competes with the capture of the organic radical by Cr(II) ions (Eq. (B)). Rearrangement of  $\text{ClH}\dot{\text{C}}\text{COOH}$  to the more stable radical  $\text{ClH}_2\text{CCOO}\cdot$  or its reaction with the solvent followed by fast association (Eq. (C)) could explain



these experimental results.

It is remarkable that  $\Delta S^\ddagger = -29.8 \pm 2 \text{ e.u.}$  for the oxidation of Cr(II) ions by trichloroacetic acid compares well with  $\Delta S^\ddagger = -32.3 \pm 2 \text{ e.u.}$  for the reaction

of Cr(II) with dichloroacetate ion and with  $\Delta S^\ddagger = -31.1 \pm 2$  e.u. for its reaction with dichloroacetic acid. Difference in oxidation rates reflects different activation enthalpies for trichloroacetic acid ( $\Delta H^\ddagger = 6.9 \pm 0.6$  kcal mol<sup>-1</sup>) and for both reaction paths in the reaction system studied ( $\Delta H^\ddagger = 0.2 \pm 0.6$  kcal mol<sup>-1</sup>). This means that the faster rate of the reaction with trichloroacetic acid at 25°C will be preserved over a broad temperature region.

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