

## OXIDATION OF Cr(II) IONS BY HYDRAZOIC ACID

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Oxidation of Cr(II) ions by hydrazoic acid in an aqueous solution of perchloric acid was studied. The second order rate constant of the reaction,  $k_B$  ( $8.9 \text{ l mol}^{-1} \text{ s}^{-1}$  at  $15^\circ\text{C}$ ), does not depend on hydrogen ion concentration and on ionic strength. The reaction rate increases moderately in the presence of  $\text{Cl}^-$ ,  $\text{Br}^-$ ,  $\text{J}^-$ , and  $\text{SO}_4^{2-}$  ions and markedly in the presence of  $\text{F}^-$  and  $\text{SCN}^-$  ions. It was found that the amount of  $\text{CrX}^{2+}$  complexes formed in the redox reaction in the presence of  $\text{X}^-$  ions exceeds that expected on the basis of reaction mechanism involving participation of  $\text{X}^-$  ions only in the rate determining interaction of Cr(II) ions with hydrazoic acid.

Reducible ligands have special position in redox reactions of Cr(III) and Co(III) complexes. For their reduction by Cr(II) ions two-step bridge mechanism of electron transfer was suggested in some cases<sup>1,2</sup>, involving the bridging ligand reduced to radical-ion as an intermediate. It seems therefore useful to study the rates and mechanism of reduction of free ligands by Cr(II) ions. An accurate agreement between the rate constants and activation parameters of the reactions of free and bonded ligands cannot be, however, expected, since reactants differ in charge and also the character of the radical-anion formed from ligands would be different.

A qualitative study of oxidation of Cr(II) ions by sodium azide revealed<sup>3</sup> that in an aqueous perchloric acid solution besides hexaquo chromium(III) ions also pentaquoamochromium(III) ions and binuclear Cr(III) complexes are formed, the nature of the products being influenced by chloride ions. In a kinetic study of reduction of hydrazoic acid by Cr(II) ions<sup>4</sup> the rate determining formation of Cr—N bond is considered as the initial step of the reaction, and reactions of intermediate products are discussed. The effect of chloride ions on the distribution of Cr(III) products is explained by redox reaction of the intermediate,  $\text{CrNH}_3^{3+}$ , formed in the rate determining step, with chloride ions, followed by coordination of the chlorine atom formed to Cr(II) ions. The rate increase observed in reductions of hydroxylamine, hydrazine, and hydrazoic acid by Cr(II) ions in the presence of halogenide ions is ascribed to competition reactions of halogenopentaquo chromium(II) ions with oxidizing agents<sup>5</sup>. The suggested mechanism does not however account for the different character of reaction products.

In the present work we confirmed kinetic results obtained by Linck<sup>4</sup> for the reduction of hydrazoic acid by Cr(II) ions in the presence of perchlorate ions employing different experimental method, and extended this study to other anions. Kinetic results were compared with structure analysis of reaction products, which proved to be useful for elucidation of mechanism of the catalysis by anions. A broader series of studied anions enabled us to present evidence for such a mechanism of the reduc-

tion of hydrazoic acid by Cr(II) ions in which anions play a role not only in the rate determining step.

## EXPERIMENTAL

**Chemicals.** Solutions of Cr(II) ions were prepared by dissolving metallic chromium (99.999% Koch-Light) in 0.5 to 1M-HClO<sub>4</sub> (Analar). The chromium was activated prior to dissolving by 6M-HCl. All solutions which were in contact with Cr(II) ions were thoroughly freed of atmospheric oxygen by a stream of nitrogen (for electric lamps). The nitrogen was purified by passing it through Cr(II) solutions prepared for this purpose by reduction of chromium(III) perchlorate with zinc amalgam. NaN<sub>3</sub> (Schuchardt, München-BRD) and the other chemicals were of analytical purity grade. Sodium salts were used in examining the effect of anions on both kinetics of the reaction and the structure of reaction products.

**Distribution of products.** Cr(III) complexes formed in the reaction were separated on a glass column (8 cm × 1 cm) filled with Dowex 50 W-X 2 (200–400 mesh) in the H<sup>+</sup> form. The complexes with the +2 charge of the type CrX<sup>2+</sup> were separated from the reaction products by elution with 0.5M-HClO<sub>4</sub>. The +3 charged complexes were eluted with 1M-HClO<sub>4</sub>. The higher charged binuclear complexes were not eluted even by 2M-HClO<sub>4</sub>. The amount of individual Cr(III) complexes in eluted bands was determined polarographically, from cathodic waves of Cr(III) complexes. The half-wave potentials depended on the character of ligands, and CrX<sup>2+</sup> complexes were presumed to have equal diffusion coefficients. The bond in a complex formed between Cr(III) and SCN<sup>-</sup> ions was determined both spectrophotometrically and polarographically. The instrument used was Specord UV VIS (Zeiss, Jena). Quartz cells were 1 cm thick. The conditions for product analysis were chosen so that the redox reaction proper was complete in a 6–7 min period. The elution time did not exceed 45 min. Subsequent aequation of CrX<sup>2+</sup> complexes did not then influence the results.

**Kinetic measurements.** Polarographic measurements were performed with a LP 55 polarograph connected to an electronic compensation recorder, Model EZ-8 (Laboratorní přístroje, Prague). The reaction vessel was Kalousek polarographic cell equipped with a temperature controlled jacket. Dropping mercury electrode (drop time 3.1 s, flow rate 2.3 mg per s<sup>-1</sup> at the height of mercury reservoir 68 cm and at zero potential) was used as measuring electrode. The reference electrode was normal calomel electrode (N.C.E.). Nitrogen atmosphere was used in all polarographic measurements, and a stream of nitrogen served also for mixing the reaction mixture.

Kinetics of reduction of hydrazoic acid by Cr(II) ions was followed polarographically, by recording time dependence of limiting diffusion anodic current of Cr(II) ions at a constant potential (in the absence of other than perchlorate anions at -0.1 V vs N.C.E.). Addition of halogenides and other studied ions to the reaction mixture shifted the half-wave potential of anodic wave of Cr(II) ions to more negative regions (the wave corresponds to electrooxidation of Cr(II) to Cr(III) and its potential is -0.35 V in 1M-HClO<sub>4</sub>), and hence for each anion a suitable potential had to be chosen. The limiting current of Cr(II) ions was found to be proportional to the ions concentration and the wave had diffusion character. The height of this wave did not change in the absence of hydrazoic acid. Of all the reactants and products, only Cr(II) ions increased current at the potential chosen.

In most kinetic measurements the sufficient excess of hydrazoic acid was used and rate constants were calculated from the integrated form of first order kinetic equation

$$\log(i_0/i) = (k_{\text{obs}}/2.3) t, \quad (1)$$

where  $i_0$  and  $i$  are the heights of the limiting current of Cr(II) ions at time  $t = 0$  and  $t$ . The second order rate constant  $2k_B$  was obtained by dividing  $k_{obs}$  with hydrazoic acid concentration. In some cases (when five to tenfold excess of hydrazoic acid was used) it was necessary to make allowance for a decrease of the acid concentration due to its reaction according to stoichiometrical equation,  $\log(i_0/i) - f(t)$  being at the same time linear. On using equivalent concentration of reactants, the rate constant  $k_B$  was determined from the graphical dependence,  $1/i$  vs  $f(t)$ . Both methods yielded comparable  $k_B$  values. The reaction was followed usually for 2 to 3 half-times. The rate constants recorded are the average of at least 3 measurements. The  $k_{obs}$ 's were determined with the accuracy of  $\pm 4.5\%$ .

## RESULTS

**Stoichiometry.** Preliminary experiments showed that the reaction between hydrazoic acid and Cr(II) ions in 0.1–1M-HClO<sub>4</sub> and a 15–30°C temperature range has half-time in seconds when reactants are used in concentrations 10<sup>-2</sup> to 10<sup>-1</sup>M. This enabled the stoichiometry of the reaction to be determined by polarometrical titration of 10<sup>-2</sup>M solution of Cr(II) ions with 0.1M-HN<sub>3</sub>. From graphical dependence of the height of limiting diffusion current of Cr(II) ions on the amount of titrating reagent added we determined the equivalent point corresponding to the stoichiometry of 2 mol of Cr(II) ions per 1 mol of hydrazoic acid.

**Kinetic measurements.** The order of the reaction with respect to Cr(II) ions was determined with sufficient excess of hydrazoic acid by integral method, from the time dependence of limiting diffusion current of Cr(II) ions. The linear dependence,  $\log(i_0/i) - f(t)$ , proves that the reaction is first order in Cr(II) ions. The rate constant  $k_{obs}$ , calculated from Eq. (1), increases linearly with concentration of the acid, which shows that the reaction is first order also with respect to the oxidizing agent. In 10<sup>-3</sup>M-Cr(II), 5 · 10<sup>-4</sup>M-HN<sub>3</sub>, and 0.9M-HClO<sub>4</sub>, the  $1/i$  vs  $t$  dependence was linear. This indicates that the overall reaction order equals 2. In the presence of perchlorate ions the reaction follows Eq. (2)



where  $k_B = 8.95 \text{ l mol}^{-1} \text{ s}^{-1}$  at 15°C. The rate constant does not depend on H<sup>+</sup> concentration for HClO<sub>4</sub> = 3 · 10<sup>-3</sup> to 0.9M and ionic strength (0.1 to 0.9). From the  $k_B$  values for temperatures 20, 30, 35, and 40°C (10.6, 14.7, 17.1, and 19.3 l mol<sup>-1</sup> s<sup>-1</sup>, respectively) the activation parameters determined from Eyring equation were:  $\Delta H^\ddagger = 4.6 \pm 0.6 \text{ kcal/mol}$ , and  $\Delta S^\ddagger = -35.6 \pm 2 \text{ cal/mol deg}$ .

Reaction rate moderately increases in the presence of SO<sub>4</sub><sup>2-</sup>, J<sup>-</sup>, Cl<sup>-</sup>, and Br<sup>-</sup> ions, whereas F<sup>-</sup> and SCN<sup>-</sup> ions exert very strong rate-enhancing effect (Fig. 1). Stoichiometry of the reaction remains 2 : 1 and also the reaction order does not change. The second order rate constant  $k_B$  can be expressed as

$$k_B = k_0 + k_x[X^-]^n. \quad (3)$$

This relation can be rewritten to the form

$$\log(k_B - k_0) = \log k_x + n \log[X^-]. \quad (4)$$

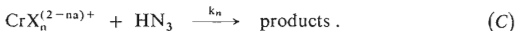
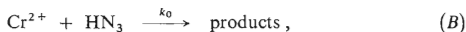
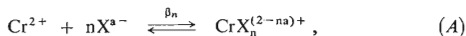
For  $F^-$  ions  $n = 2$ , for the other anions  $n = 1$ . Mean values of  $k_x$  ( $1^2 \text{ mol}^{-2} \text{ s}^{-1}$ ), calculated according to relations (3) and (4) are:  $\text{SO}_4^{2-}$  0.62,  $\text{I}^-$  2.5,  $\text{Cl}^-$  7.7,  $\text{Br}^-$  12.5,  $\text{SCN}^-$  144,  $F^-$  286.

*Product analysis.* In the absence of anions, except perchlorate ions, the formation of complexes with the charge less than +3 was not observed. Complexes  $\text{CrX}^{2+}$  were however formed in a solution of  $10^{-2} \text{M-HN}_3$ ,  $10^{-2} \text{M-Cr(II)}$ , and  $0.1 \text{M-HClO}_4$  in the presence of  $\text{Cl}^-$ ,  $\text{Br}^-$ ,  $\text{J}^-$ ,  $\text{SO}_4^{2-}$ , and  $\text{SCN}^-$  ions. Fluoride ions did not affect the structure of the products. The amount of  $\text{CrX}^{2+}$  ions formed depended on concentration of anions  $X^-$  (Fig. 2). The amount of Cr(III) complexes with the +3 charge decreased with increasing  $X^-$  concentration. Half-wave potentials of  $\text{CrX}^{2+}$  complexes, which were eluted from the ion exchanger with  $0.5 \text{M-HClO}_4$ , were for  $\text{J}^- = -0.37 \text{ V}$ ,  $\text{Br}^- = -0.44 \text{ V}$ ,  $\text{Cl}^- = -0.77 \text{ V}$ ,  $\text{SCN}^- = -0.82 \text{ V}$ , and  $\text{SO}_4^{2-} = -0.90 \text{ V}$  (vs N.C.E.), in good agreement with reported data<sup>6</sup>.

## DISCUSSION

As follows from the rate equation, the oxidation of Cr(II) ions by hydrazoic acid in an aqueous  $\text{HClO}_4$  solution proceeds *via* an activated complex which contains 1 molecule of  $\text{HN}_3$  and 1 molecule of the reducing agent. As stoichiometry of the reaction requires the consumption of two moles of Cr(II) ions per one mol of the oxidizing agent, and the reaction is at the same time first order in both reactants, the reaction mechanism should involve formation of transient oxidation states of one of the two reactants, likely nitrogen, according to the scheme proposed by Linck<sup>4</sup>. As far as numerical values are concerned, there is a good agreement between rate constants determined by us and by Linck<sup>4</sup> for  $15^\circ \text{C}$  and the medium containing only perchlorate ions, although the activation enthalpy,  $\Delta H^\ddagger = 7.1 \text{ kcal mol}^{-1}$  reported in work<sup>4</sup> is slightly higher, and the activation entropy,  $\Delta S^\ddagger = -29 \text{ cal mol}^{-1} \text{ deg}^{-1}$  is more positive. On the contrary, the activation parameters reported by Wells and Salam<sup>5</sup> differ from the above data. The low values of the activation enthalpy are in accordance with a process requiring only small changes in the arrangement of primary or secondary hydration sphere prior to the electron process.

Rate constant  $k_B$  depends on concentration of halogenide and other ions according to Eq. (3). The  $k_0/k_x$  ratio ( $1 \text{ mol}^{-1}$ ), determined from kinetic results is 15 for  $\text{SO}_4^{2-}$ , 3.6 for  $\text{J}^-$ , 1.2 for  $\text{Cl}^-$ , 0.72 for  $\text{Br}^-$ , 0.062 for  $\text{SCN}^-$ , and 0.031 for  $F^-$  ions. The effect of these anions on reaction rate can be explained by formation of complexes between  $\text{Cr}^{2+}$  and  $X^-$  ions (Eq. (A)) which then react with hydrazoic acid at a faster rate than do hexaaquochromium(II) ions, *i.e.*  $k_n > k_0$  according to equations (B) and (C).



Dependence of the rate constant  $k_B$  on  $\text{X}^{a-}$  concentration can be then expressed as

$$k_B = \frac{k_0 + \sum_n k_n \beta_n [\text{X}^{a-}]^n}{1 + \sum_n \beta_n [\text{X}^{a-}]^n}. \quad (5)$$

The  $k_B$  vs  $[\text{X}^{a-}]^n$  plot is nearly linear, with  $n = 1$  for  $\text{Cl}^-$ ,  $\text{Br}^-$ ,  $\text{J}^-$ ,  $\text{SO}_4^{2-}$ , and  $\text{SCN}^-$  ions and with  $n = 2$  for  $\text{F}^-$  ions. This indicates that formation of  $\text{Cr(II)}$  complexes containing the greater number of ligands is negligible (with the exception of  $\text{F}^-$  ions)

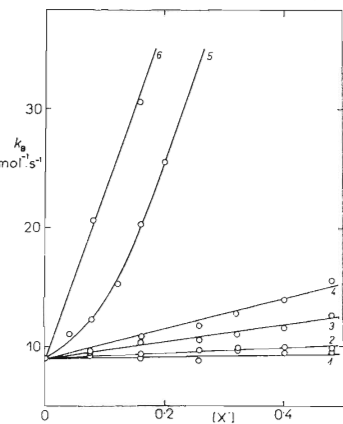


FIG. 1

Effect of  $\text{X}^-$  Concentration on Rate Constant  $k_B/1 \text{ mol}^{-1} \text{ s}^{-1}$

1  $\text{SO}_4^{2-}$ , 2  $\text{J}^-$ , 3  $\text{Cl}^-$ , 4  $\text{Br}^-$ , 5  $\text{F}^-$ , 6  $\text{SCN}^-$ ,  $10^{-4} \text{M-Cr(II)}$ ,  $5 \cdot 10^{-4} \text{M-NaN}_3$ ,  $0.2 \text{M-HClO}_4$ , temperature  $15^\circ \text{C}$ , ionic strength 0.76.

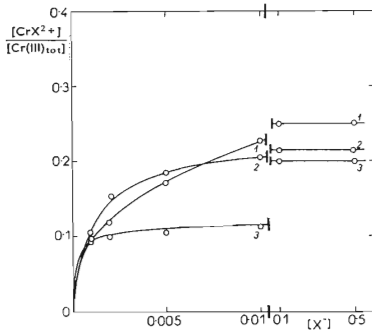


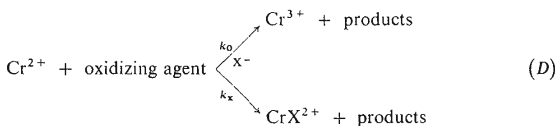
FIG. 2

Dependence of the Amount of  $\text{CrX}_2^+$  Complexes on Concentration of  $\text{Cl}^-$  (curve 1),  $\text{Br}^-$  (curve 2), and  $\text{J}^-$  (curve 3) Ions

compared to  $\text{CrX}^{(2-a)+}$  complexes. Numerical values of  $k_x$  (which is in fact association constant  $\beta$  multiplied by corresponding rate constant of the associate with  $\text{HN}_3$ ) for halogenide ions show that the parallel reaction path involving activated complex of the type  $[\text{XCrN}_3\text{H}^+]^*$  does not increase significantly the rate of the reduction of hydrazoic acid by Cr(II) ions when  $\text{X} = \text{J}^-, \text{Br}^-, \text{and Cl}^-$ . This finding is in harmony with the known<sup>4</sup> effect of  $\text{Cl}^-$  ions and extends the validity of this observation to other ions. On the other hand, it does not allow to determine sufficiently accurate values of association constants between  $\text{Cr}^{2+}$  ions and halogenides, as attempted by Wells and Salam<sup>5</sup>.

The effect of halogenide ions manifests itself in distribution of Cr(III) complexes. Already in  $10^{-3}\text{M}$  solutions of  $\text{Cl}^-$ ,  $\text{Br}^-$ , and  $\text{J}^-$  ions, the  $\text{X}^-$  ion enters the primary coordination sphere of formed Cr(III) complexes. The amount of  $\text{CrX}^{2+}$  ions increases with increasing concentration of  $\text{X}^-$  ions, with the exception of  $\text{F}^-$  ions, while the amount of hexaaquochromium(III) ions decreases.

Assuming two parallel reactions

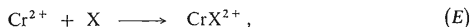


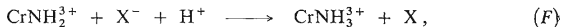
one obtains

$$1/F_x = ([\text{CrX}^{2+}] + [\text{Cr}^{3+}])/[\text{CrX}^{2+}] = 1 + (k_0/k_x)[\text{X}^-]^{-1}. \quad (6)$$

From the dependence  $1/F_x = f([\text{X}^-]^{-1})$ , which was linear for  $\text{Cl}^-$  and  $\text{Br}^-$  ions, the  $k_0/k_x$  ratio for  $\text{Cl}^-$  and  $\text{Br}^-$  ions was found to be  $1.1 \cdot 10^{-3}$  and  $7.3 \cdot 10^{-4} \text{ mol}^{-1}$ , respectively. As follows from comparison of these values with data obtained from kinetic results the differences are much greater than experimental errors. The extraordinarily high value of  $k_x$ , relative to  $k_0$ , does not correspond, however, to reducing ability of  $\text{CrX}^+$  ions, when compared with hexaaquochromium(II) ion<sup>7</sup>.

As the rate of the oxidation of Cr(II) ions by hydrazoic acid is not significantly influenced by  $\text{Cl}^-$ ,  $\text{Br}^-$ , and  $\text{J}^-$  ions, unlike the product distribution, the above ions have to react with an intermediate which is formed in or after the rate determining step. The  $\text{CrX}^{2+}$  complexes may be assumed to be formed by reaction of  $\text{Cr}^{2+}$  ions with atom X (Eq. (E)) which arises from the oxidation of  $\text{X}^-$  by the intermediate product. Such capture of halogenide ions by Cr(II) ions is very efficient<sup>8</sup>. It seems then probable that the reaction (F) competes





with other reactions of  $\text{CrNH}_2^{3+}$  in the presence of  $\text{X}^-$  ions, and its rate increases with increasing concentration of  $\text{X}^-$ . As the result,  $\text{CrNH}_3^{3+}$  and  $\text{CrX}^{2+}$  complexes are major products at higher  $\text{X}^-$  concentrations. These conclusions are also supported by the observed effect of  $\text{F}^-$  ions. Although they exhibit strongest effect on the rate of the reduction of hydrazoic acid,  $\text{CrF}^{2+}$  complexes are not formed. This agrees with the fact that  $\text{J}^-$ ,  $\text{Br}^-$ , and  $\text{Cl}^-$  ions are more easily oxidized than are  $\text{F}^-$  ions.

The suggested mechanism is further supported by the results obtained for the oxidation of Cr(II) ions by hydrazoic acid in the presence of  $\text{SCN}^-$  ions. The absorption spectrum of the fraction of Cr(III) complexes eluted from the ion exchanger with 0.5M- $\text{HClO}_4$  showed maxima at 305, 407, and 558 nm. Their polarographic cathodic wave had  $E_{1/2} = -0.82 \text{ V vs N.C.E.}$  This indicates that the fraction contains mostly  $\text{CrNCS}^{2+}$  isomer. Providing that  $\text{SCN}^-$  ions participate only in the rate-determining step, they must function in further reactions as a bridging ligand, and the  $\text{CrSCN}^{2+}$  isomer could be then expected as the reaction product.

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