

INFLUENCE OF SOLVENT ON KINETICS OF REACTIONS OF Cr(II) IONS

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This paper deals with the study of redox reactions of Cr(II) ions with hydroxylamine, hydrazoic acid, maleic acid, di- and trichloroacetic acids in so-called typically aqueous mixtures of water with methyl alcohol, isopropyl alcohol, or tert-butyl alcohol. The kinetics of the redox reaction with dichloroacetic acid was studied also in the medium of aqueous acetone and in a typically nonaqueous medium water-acetonitrile. The dependences of activation Gibbs energies on the mole fraction of the nonaqueous component have no minima and maxima characteristic for the thermodynamic behaviour of the mentioned binary systems. However, the change of the activation Gibbs energy with the mole fraction of tert-butyl alcohol is not monotonous with all the studied reactions of Cr(II) ions. At a constant mole fraction of the nonaqueous component, the usual trend of the influence on the rate constants decreases in the sequence tert-butyl alcohol > isopropyl alcohol > methyl alcohol. Tert-butyl alcohol hinders most strongly the redox reaction with trichloroacetic acid, whereas it accelerates the reaction of Cr(II) ions with maleic acid and hydroxylamine.

The influence of the solvent mainly on the kinetics of substitution reactions whose reaction mechanism was in substance known was investigated very thoroughly¹⁻³. Among these were reactions with a dissociation mechanism, such as solvolysis of tert-butyl chloride, and association reactions, such as alkaline hydrolysis of organic halides. The possibility to use the solvent effect on the reaction kinetics in diagnosis of the mechanism of inorganic substitution⁴ and redox^{5,6} reactions has been considered recently. Further progress toward a quantitative theory of the solvent effect on the reaction kinetics and mechanism requires to study the reaction kinetics in a broad range of aqueous-nonaqueous solvents as a function of their composition.

The present work deals with the study of the kinetics of redox reactions of Cr(II) ions with hydroxylamine, hydrazoic acid, maleic acid, di- and trichloroacetic acids in so-called typically aqueous mixtures (TA) of water with methyl alcohol, isopropyl alcohol, or tert-butyl alcohol. The kinetics of the redox reaction of Cr(II) ions with dichloroacetic acid was also studied in the systems water-acetone (TA) and water-acetonitrile (typically nonaqueous positive, TNAP). Our work is a continuation of the kinetic study of the oxidation mechanism of Cr(II) ions with the mentioned oxidants in aqueous solutions of perchloric acid⁷⁻¹¹.

EXPERIMENTAL

Chemicals. Solutions were prepared from reagent grade chemicals and distilled water. The nonaqueous solvents were distilled prior to use. Aqueous solutions of Cr(II) ions were prepared by dissolving an excess quantity of Cr (99.999%, Koch Light) in 0.1—1M-HClO₄ in nitrogen

TABLE I

Influence of solvent on rate constant k (dm³ mol⁻¹ s⁻¹) for reaction of Cr(II) ions with NH₂OH (A), HN₃ (B), maleic acid (C), CHCl₂COOH (D), and CCl₃COOH (E) in 1M-HClO₄. Temperature: 298 K (A—D), 293 K (E)

x_2	$10^3 \cdot k_A$	k_B	$10^2 \cdot k_C$	$10^2 \cdot k_D$	k_E
Methyl alcohol					
0.049	9.23	8.13	6.19	9.46	6.19
0.076	—	7.98	—	—	—
0.105	9.83	7.85	6.14	9.19	6.13
0.169	10.70	7.41	6.05	8.51	6.08
0.242	11.85	7.00	5.84	8.48	6.01
0.327	10.96	6.03	5.52	7.31	5.79
0.427	10.55	4.79	5.03	6.41	5.23
0.547	8.85	4.32	4.14	6.02	4.21
0.693	6.14	2.63	2.67	4.55	3.58
Isopropyl alcohol					
0.005	—	5.96	—	—	—
0.012	—	4.57	—	—	—
0.027	9.83	4.47	7.15	9.61	6.10
0.058	12.43	4.27	7.84	8.53	5.37
0.096	15.25	4.17	8.02	7.48	4.12
0.144	19.88	3.98	8.81	5.75	2.57
0.204	25.76	3.80	9.01	5.26	1.80
0.282	32.10	3.63	10.38	3.57	1.55
0.388	41.40	3.47	11.83	2.99	1.27
0.541	45.92	3.24	13.89	2.57	1.06
Tert-butyl alcohol					
0.022	8.88	6.84	6.46	8.92	5.42
0.048	10.57	5.62	6.74	8.14	5.29
0.081	12.45	5.25	7.50	6.16	3.31
0.121	16.52	4.90	7.74	4.46	1.90
0.173	19.96	4.62	8.37	3.36	1.14
0.244	23.52	3.94	9.81	2.75	1.02
0.343	36.75	3.67	12.24	2.36	0.98
0.493	57.50	2.82	18.75	1.91	0.87

atmosphere, in which all kinetic measurements were done. The quantity of Cr(III) in these solutions was determined polarographically from the ratio of the height of the anodic wave of Cr(II) ($E_{1/2} = -0.36$ V vs N.C.E. in 1M-HClO₄) to the cathodic wave of Cr(III) ($E_{1/2} = -0.98$ V vs N.C.E. in 1M-HClO₄). The content of Cr(III) in the analysed solutions was 7% on the average.

Analyses. In the reaction of Cr(II) with dichloroacetic acid, we determined the yields of primary Cr(III) products important with respect to the assessment of the reaction mechanism. The complexes formed by the redox reaction in mixtures of water with methyl alcohol, isopropyl alcohol, tert-butyl alcohol, acetone, and acetonitrile were separated by chromatography on ion exchangers. We used glass columns (10 × 1 cm) filled with Dowex 50W-X2 (200–400 mesh) in the H⁺ form; the method of separation, spectrophotometric identification, and determination of primary Cr(III) products were the same as for the reaction in the medium of aqueous perchloric acid¹⁰. Cr(H₂O)₅Cl²⁺ ions were found to be the green primary products of the redox reaction of Cr(II) with dichloroacetic acid in all media under study. The molar ratio of the formed CrCl²⁺ complex to all Cr(III) products was in 50 vol.% methyl alcohol 0.46, in isopropyl alcohol 0.43, in tert-butyl alcohol 0.44, in acetone 0.44, and in acetonitrile 0.43.

Kinetics. The kinetics of oxidation of Cr(II) ions was followed polarographically in all media under study. The time dependence of the limiting anodic diffusion current of Cr(II) was recorded at 0 V in mixtures with methyl alcohol, at +0.2 V with isopropyl alcohol, tert-butyl alcohol, and acetone, and at +0.1 V with acetonitrile (against N.C.E.). The polarograph was of the type LP 7e (Laboratorní přístroje, Prague) with a normal calomel reference electrode and a dropping mercury electrode. The measured solutions were placed in a tempered Kalousek cell. The current at the chosen potential was due only to Cr(II) ions. The oxidants were in excess and the rate constants k_{exp} were evaluated from the linearized first-order kinetic equation, $\log(I_0/I) = f(t)$, where I_0 is the limiting diffusion current of Cr(II) at the beginning of the reaction and I that at time t . The second-order rate constant, k , was obtained by dividing k_{exp} by the oxidant concentration and a stoichiometric factor of 2. A correction for the concentration drop of HN₃ according to the stoichiometrical equation was necessary for the reaction with hydroazotic acid, then the reaction proceeded with a constant half-time. The reactions were followed during about three half-times and the given values of the rate constants are averages from three measurements (accuracy ± 5%, in reaction with HN₃ ± 7%).

Based on the Eyring's theory of absolute reaction rates, the activation Gibbs energies were calculated from the rate constants and temperatures for various mole fractions x_2 of the nonaqueous solvent. The values for $x_2 = 0$ are in good agreement with published data for aqueous solutions of perchloric acid⁷⁻¹¹.

RESULTS AND DISCUSSION

The change of the activation Gibbs energy ΔG^\ddagger for a reaction in aqueous and in mixed a queous–nonaqueous medium can be expressed as

$$\delta_{r_1} \Delta G^\ddagger = \Delta G_{x_2}^\ddagger - \Delta G_{(x_2=0)}^\ddagger.$$

In the cases under study, the solubility of Cr(II) ions is influenced by the addition of the nonaqueous component whose increasing mole fraction x_2 can lead to their stabilization. This would result in an increase of the value of $\delta_m \Delta G^\ddagger$ and hence

to a decrease of the rate constant with increasing x_2 . Such a behaviour was indeed observed in redox reactions of Cr(II) with hydrazoic, di- and trichloroacetic acids in water-alcohol mixtures; and in the case of dichloroacetic acid also in water-acetone and water-acetonitrile mixtures. The results are shown in Fig. 1 and Table I. The reaction rate of Cr(II) ions with maleic acid is lowered by the addition of methyl alcohol but enhanced by the addition of isopropyl or tert-butyl alcohol. In the redox reaction with hydroxylamine, the rate constant is increased by increasing concentration of isopropyl alcohol or tert-butanol whereas acetonitrile slows down the reaction and methyl alcohol has an accelerating effect up to a mole fraction of 0.245; further it hinders the reaction.

In redox reactions of U^{3+} ions with hydrazoic acid¹², dichloroacetic acid¹³, and trichloroacetic acid¹⁴, the effect on the reaction rate (not its character) decreases in the order: tert-butyl alcohol > isopropyl alcohol > methyl alcohol at equal mole fractions of the nonaqueous component. The same trend was observed in the studied reactions of these oxidation agents with Cr(II) ions. The decrease of the

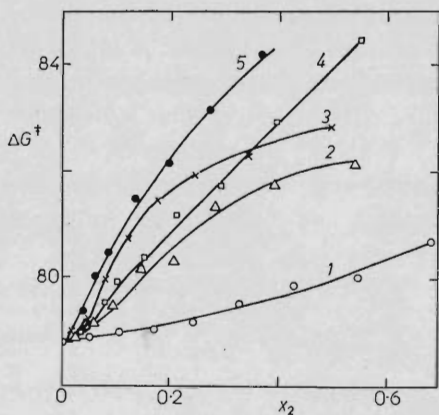


FIG. 1

Dependence of activation Gibbs energy ΔG^\ddagger (kJ/mol) on mole fraction of nonaqueous solvent x_2 in reaction of Cr(II) ions with CHCl_2COOH . 1 Methyl alcohol, 2 isopropyl alcohol, 3 tert-butyl alcohol, 4 acetone, 5 acetonitrile

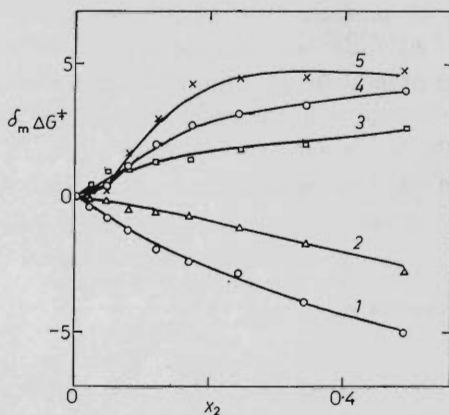


FIG. 2

Influence of tert-butyl alcohol (mole fraction x_2) on reaction rate (expressed by change of $\delta_m \Delta G^\ddagger$ in kJ/mol) of Cr(II) ions. Reaction with: 1 NH_2OH , 2 CCl_3COOH , 3 CHCl_2COOH , 4 HN_3 , 5 maleic acid

reaction rate of Cr(II) with dichloroacetic acid in the TNAP mixture is still more marked than in water-alcohol mixtures at the same x_2 values. In redox reactions of Cr(II) ions, the nonaqueous solvent slows down the redox reaction (with maleic acid and hydroxylamine, isopropyl alcohol and tert-butyl alcohol accelerate) without a minimum, which is most marked in tert-butyl alcohol at $x_2 = 0.05$ in redox reactions of U^{3+} ions with trichloroacetic acid¹⁴, dichloroacetic acid¹³ and hydrazoic acid¹². The authors⁶ conclude that typical curves of a sigmoidal shape are characteristic for redox reactions of U^{3+} ions with an outer-sphere mechanism.

The increase of ΔG^\ddagger with increasing x_2 of tert-butyl alcohol is not in all studied reactions of Cr(II) ions monotonous (Fig. 2). The values of $\delta_m \Delta G^\ddagger$ at its mole fraction $x_2 = 0.493$ are 4.81, 4.09, 2.65, -2.66, and -4.90 kJ/mol in reactions with CCl_3COOH , $CHCl_2COOH$, HN_3 , maleic acid, and hydroxylamine, respectively. The influence of methyl alcohol on $\delta_m \Delta G^\ddagger$ is in the studied reactions of Cr(II) ions monotonous except for NH_2OH and at $x_2 = 0.493$ this quantity lies between 1.5 kJ/mol for HN_3 and -0.3 kJ/mol for NH_2OH .

The redox reactions of Cr(II) ions with the mentioned oxidation agents in aqueous solutions of $HClO_4$ have an inner-sphere mechanism^{7-11,15}. The transfer of a Cl atom from di- or trichloroacetic acid to Cr(II) was proved^{10,11}. The bridge structure of the activated complex^{7,15} is considered also in the case of hydroxylamine, but in the medium of aqueous $HClO_4$ the protonized form of NH_2OH is considered dominant, which is possibly responsible for its different behaviour in binary mixtures. In aqueous-nonaqueous mixtures, the principal features of the mechanism of the reaction of Cr(II) ions with dichloroacetic acid are not changed. The reaction is still of the first order with respect to both reactants and the yields of $CrCl^{2+}$ complexes (primary products) are in the range 43-46% of the total Cr(III) products. This is in accord with the formation of a bridge structure Cr-Cl-C also in the medium of 50 vol.% methyl, isopropyl, or tert-butyl alcohol, acetone, and acetonitrile; the reaction mechanism remains inner sphere in all studied TA and TNAP binary mixtures.

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