

KINETICS OF OXIDATION OF Cr(II) IONS BY SALICYLALDEHYDE

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Kinetics of oxidation of Cr(II) ions by salicylaldehyde were studied in water-methanol-perchloric acid and water-acetic acid-perchloric acid systems. The reaction was first order both in Cr(II) ions and salicylaldehyde concentrations. The rate constant was inversely proportional to hydrogen ions concentration, which indicates that a reaction path involving formation of a dissociated or protonated form of salicylaldehyde plays an important role. Formation of extremely stable Cr(III) complex is discussed. Activation parameters of the reaction are reported.

While the possibility of reducing some aromatic aldehydes with Cr(II) ions has been known for a long time¹, the reaction most frequently studied was reduction of benzaldehyde with Cr(II) ions¹⁻³. In the studies just mentioned formation of organochromium(III) complexes as reaction intermediates has been suggested. A more detailed study of the kinetics of the oxidation of Cr(II) ions by salicylaldehyde has not yet been performed and is the subject of the present work.

EXPERIMENTAL

Chemicals. Salicylaldehyde *p.a.* (Lachema, Brno) was distilled before use under nitrogen and the medium fraction was collected, b.p. 86°C/18 Torr. Solution of Cr(II) ions was prepared by dissolving metallic chromium (99.999%, Koch-Light) in perchloric acid of required concentration (usually 0.5–1M) under nitrogen atmosphere. The chromium was first activated in 6M-HCl. All solutions which were to be in contact Cr(II) ions were thoroughly deoxygenated by a stream of nitrogen (for electric lamps). The nitrogen was purified by passing through solutions of Cr(II) ions which were prepared by reduction of c. 1M chromium(III) perchlorate with zinc amalgam. Methanol (*p.a.*) was rectified before use. The following chemicals (*p.a.*) were used without further purification: perchloric acid (Apolda), sodium perchlorate (Fluka A.G., Buchs), chromium(III) perchlorate (Serva International), and sodium chloride (Lachema, Brno).

Cr(III) complexes formed were isolated by chromatography on Dowex 50W-X2 (200 to 400 mesh). By extraction with n-hexane the aqueous layer of the reaction mixture was separated, the portion of which was introduced on the column of an ion exchange resin in the H⁺ form (8 cm × 1 cm). A solution of Cr(ClO₄)₃·6H₂O was used as standard. This Cr(III) complex with charge 3+ was quantitatively eluted with 1M-HClO₄ in 52 min. Several attempts have been made to isolate Cr(III) products in solid state. A solution of 0.75M-Cr(II), 0.66M salicylaldehyde in 43% methanol and 10⁻²M-HClO₄ was allowed to stand in a nitrogen atmosphere for 2 days. After extraction with n-hexane, the reaction mixture was evaporated nearly to dryness on an air bath. The residue was dissolved in methanol, filtered and crystallized to give yellow-brown

crystals. The product was inhomogeneous under microscope and contained macroscopically inseparable light yellow crystals with m.p. 154°C and a dark brown admixture which sintered above 250°C. For this reason the results of elemental analysis (3.84% H, 42.19% C) cannot be considered as reliable.

Spectroscopic and polarographic measurements. Spectrophotometric measurements were carried out on a Specord spectrophotometer (Zeiss, Jena). The reaction was performed at 25°C in 0.5 cm (360–500 nm region) or 3 cm sealed quartz cells (500–800 nm region). Polarographic measurements were carried out on LP 7 Polarograph (Laboratorní přístroje) using Kalousek polarographic cell thermostated with water with an accuracy of $\pm 0.1^\circ\text{C}$. Standard calomel electrode was used as reference electrode. Indication electrode was mercury dropping electrode with time of drop 4 s and a flow rate of 1.85 mg s^{-1} at the mercury column height of 54 cm at zero potential. All measurements were made under nitrogen.

Kinetics of oxidation of Cr(II) ions by salicylaldehyde was measured (because of poor solubility of salicylaldehyde in water) in water–methanol–perchloric acid and water–acetic acid–perchloric acid systems. Time dependence of limiting diffusion anodic current of Cr(II) ions at the constant potential of +0.1 V against s.c.e. was recorded. Of all the reactants and products, only Cr(II) ions increased the current at this potential. In the absence of salicylaldehyde the height of Cr(II) ion wave did not change with time. In all runs salicylaldehyde was used in sufficient excess (50–100) and therefore k_{obs} that are the product of second-order rate constant k_{B} and salicylaldehyde concentration were calculated by differential method from initial reaction rates (Eq. (1))

$$k_{\text{obs}} = \left| \left(-\frac{d[\text{Cr(II)}]}{dt} \right)_{t=0} \frac{1}{[\text{Cr(II)}]_0} \right| = \left| \left(\frac{di}{dt} \right)_{t=0} \frac{1}{i_0} \right|, \quad (1)$$

where i_0 is limiting diffusion current of Cr(II) ions at the beginning of the reaction). Prepared k_{obs} 's were determined with an accuracy of ± 6 per cent and are average of at least 3 measurements. The calculation of the rate constants from the integrated form of first-order equation did not prove good due to deviations caused by rate-retarding effect of formed Cr(III) ions⁴.

RESULTS AND DISCUSSION

Spectrophotometric investigation of the reaction of Cr(II) ions with salicylaldehyde in 48% methanol showed changes of the light blue colour of Cr(II) ions to yellow (Fig. 1). After the redox reaction had taken place, the absorption curve showed maxima at 411 nm and 582 nm which are characteristic for Cr(III) complexes. The intensity of the first band ($\epsilon_{411} 1.1 \cdot 10^3 \text{ l mol}^{-1} \text{ cm}^{-1}$, $\epsilon_{582} 19.5 \text{ l mol}^{-1} \text{ cm}^{-1}$) excludes hexaquo chromium(III) ions ($\epsilon_{410} 15.6 \text{ l mol}^{-1} \text{ cm}^{-1}$) as possible products of the redox reaction. It indicates further that organochromium(III) complexes with Cr–C bond are likely formed which exhibit extremely strong absorption⁵ in the 380–410 nm region. The bright yellow colour of the reaction mixture is preserved even during several weeks. Substitution inertness of such complexes is known. Although they are usually readily oxidized⁵, the product of the redox reaction of Cr(II) ions with salicylaldehyde did not undergo oxidation both with air oxygen

and with Fe(III) ions. Acetic acid accelerates protolysis of benzylchromium(III) and similar ions^{5,6}. We therefore studied the reaction of Cr(II) ions with salicylaldehyde in 50% acetic acid. The yellow Cr(III) complex formed was however stable even under these conditions.

The charge of formed Cr(III) complexes was determined by means of chromatography on ion exchangers. A solution of $5 \cdot 10^{-3} \text{M-Cr(II)}$ and $5 \cdot 10^{-2} \text{M}$ salicylaldehyde was reacted in $5 \cdot 10^{-2} \text{M-HClO}_4$ and 50% methanol for 2 h. Unreacted Cr(II) ions were oxidized with air oxygen and the free organic fraction was removed by extraction with n-hexane. The reaction mixture was eluted successively with 0.5, 1, 2, and 4M-HClO₄. The two bands separated on the column: a yellow band and a green one. 1M-HClO₄ that elutes from Dowex 50W - X2 complexes⁷ with +3 charge was needed for elution of the former while the latter was removed from the column only by elution with 4M-HClO₄. Relative amounts of Cr(III) complexes contained in both bands depended on the time of the redox reaction between Cr(II) ions and salicylaldehyde in nitrogen atmosphere. On prolonged reaction time, the amount of the green complex decreased. We assume that the green Cr(III) complex is the product of oxidation of unreacted Cr(II) ions with air oxygen, in fact the binuclear complex⁸ Cr₂(OH)₂⁴⁺. The product of the redox reaction proper is the yellow Cr(III) complex. The rate of its elution corresponded to that of the standard solution of Cr(III) ions with the +3 charge. In order to determine the stoichiometry of the reaction of Cr(II) ions with salicylaldehyde, we prepared a solution containing 0.5M-Cr(II), 0.2M salicylaldehyde and 0.6M-HClO₄ in 43% methanol. After the reaction had been carried out at 25°C for 4 days, it was found polarographically that

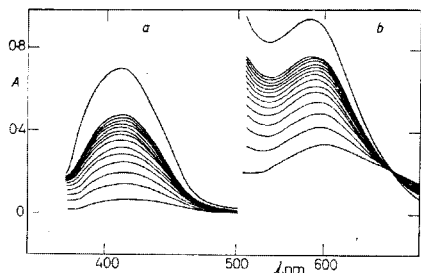


FIG. 1

Spectrophotometric Investigation of Reaction of Cr(II) Ions with Salicylaldehyde in 50% v. Methanol

0.1M Salicylaldehyde, 0.5M-HClO₄, 298 K, recorded after 106 s, the last curve after 24 h. a $1.3 \cdot 10^{-3} \text{M-Cr(II)}_0$, 0.5cm -cell; b $1.8 \cdot 10^{-2} \text{M-Cr(II)}_0$, 3 cm-cell.

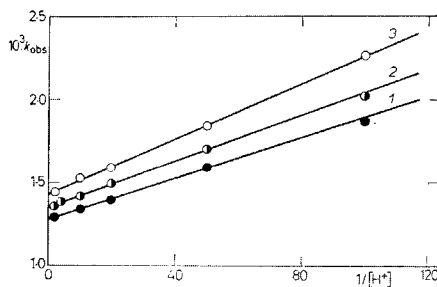


FIG. 2

Dependence of Experimental Rate Constant k_{obs} on Reciprocal Hydrogen Ion Concentration

48% v. Methanol, $3 \cdot 10^{-3} \text{M-Cr(II)}_0$, 0.1M salicylaldehyde. 1 287 K, 2 298 K, 3 313 K.

$4.8 \cdot 10^{-2} \text{M-Cr(II)}$ ions did not react. This shows that the stoichiometry requires two moles of Cr(II) ions per one mole of salicylaldehyde.

The kinetic study of the redox reaction between Cr(II) ions and salicylaldehyde was complicated by rate-retarding effect of Cr(III) ions formed. It was found by differential method from initial reaction rates that the reaction is first-order in both Cr(II) ions and salicylaldehyde concentrations⁴. In the reduction of benzaldehyde with Cr(II) ions the form of the dependence of the rate constant on hydrogen ions concentration was found³ to depend strongly on the solvent used. With methanol as solvent the rate constant of the reduction of salicylaldehyde with Cr(II) ions decreases with increasing $[\text{H}^+]$ (Fig. 2). A similar dependence has also been found in acetic acid (Table I). From the dependence of the rate constant on $[\text{H}^+]$ (Eq. (2))

$$k_{\text{B}} = k' + k''/[\text{H}^+] \quad (2)$$

the values of k' and k'' for the solvent methanol have been determined for several temperatures (Table II). In acetic acid and at 298 K, k' and k'' equaled to $3 \cdot 10^{-3} \text{ l mol}^{-1} \text{ s}^{-1}$ and $2.17 \cdot 10^{-4} \text{ l}^2 \text{ mol}^{-2} \text{ s}^{-1}$, respectively. By means of Eyring equation the following activation parameters were calculated for the path independent of $[\text{H}^+]$: $E^{\ddagger} = 0.8 \pm 0.7 \text{ kcal mol}^{-1}$ and $\Delta S^{\ddagger} = -66 \pm 3 \text{ e.u.}$ For the reaction path expressing the inverse dependence on $[\text{H}^+]$: $E''^{\ddagger} = 2.2 \pm 0.8 \text{ kcal mol}^{-1}$ and $\Delta S''^{\ddagger} = -72 \pm 3 \text{ e.u.}$ for 48% methanol and an ionic strength of 0.5. These values are similar to those obtained for the reduction of benzaldehyde with Cr(II) ions³.

The dependence of the rate constants on $[\text{H}^+]$ can be explained by assuming that reaction mechanism involves a fast equilibrium step in which protons are

TABLE I

Dependence of k_{obs} (s^{-1}) on H^+ Concentration in 50% v. Acetic Acid
 $3 \cdot 10^{-3} \text{M-Cr(II)}_0$, 0.1M salicylaldehyde, ionic strength 0.5, 298 K.

No	$[\text{HClO}_4]$	$k_{\text{obs}} \cdot 10^4$
1	0.006	22.7
2	0.02	14.6
3	0.05	8.01
4	0.1	5.42
5	0.5	4.04

TABLE II

Rate Constants k' ($\text{l mol}^{-1} \text{ s}^{-1}$) and k'' . ($\text{l}^2 \text{ mol}^{-2} \text{ s}^{-1}$) Calculated from Eq. (2)
 48% v. Methanol, 0.1M salicylaldehyde, $3 \cdot 10^{-3} \text{M-Cr(II)}$.

T, K	$10^2 \cdot k'$	$10^5 \cdot k''$
287	1.29	6.1
289	1.35	7.0
313	1.44	8.4

produced and which precedes the rate-determining step. The origin of protons cannot be looked for in hydrolysis of hexaquo chromium(II) ions⁸. A many of redox reactions of Cr²⁺ ions do not depend on H⁺ concentration, which shows both limited scope and kinetic unimportance of hydrolysis reaction. Recent works on electrochemical reductions of aldehydes stressed the importance of dissociated and protonated hydrated forms of aldehydes⁹. Although the extent of hydration of aromatic aldehydes is as a rule small compared to aliphatic aldehydes, these effects may be still important^{10,11}. The values of corresponding equilibrium constants for salicylaldehyde are not however known. This renders it impossible to estimate rate constants of the reaction of dissociated and protonated form of hydrated salicylaldehyde with Cr(II) ions as well as to decide whether this assumption is valid in this case.

A reaction which might produce protons can be also association reaction of Cr²⁺ ions with the oxidizing agent¹². In the case of salicylaldehyde that contains a system of conjugated bonds and is capable of forming chelates, this alternative seems attractive. The reaction of formed associate with additional Cr(II) ion cannot be, however, rate-determining step, since the actual reaction order with respect to Cr(II) ions is one and therefore conversion of the associate has to be fast.

In a study on the reduction of benzaldehyde with Cr(II) ions the authors postulated a bridging mechanism of the reaction². It was found that in the presence of Cl⁻ ions there proceeds transfer of chlorine atom to primarily formed Cr(III) products². The rate of the reduction of salicylaldehyde with Cr(II) ions in 0.5M-HCl 50% methanol system does not differ from that found in the absence of Cl⁻ ions. On the other hand, we observed that in a solution of 0.1M salicylaldehyde, 3 · 10⁻³M-Cr(II), 0.5M-HCl in 50% methanol, the green Cr(III) complex is formed which is eluted from H⁺ Dowex 50W-X2 already with 0.5 M-HClO₄. Its amount does not exceed approx. 30% of the total amount of Cr(III) products. It seems highly probable that this complex is Cr(III)Cl²⁺. As the rate of the redox reaction between salicylaldehyde and Cr(II) ions is not influenced by Cl⁻ ions, whereas the nature of products is affected, Cl⁻ ions have to react with an intermediate product which is formed in or after the rate-determining step. At present, it would be premature to suggest reaction scheme for the reduction studied. Experimental results indicate similarities with the reduction of benzaldehyde with Cr(II) ions but show also some important differences which should be depicted in the reaction mechanism.

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