Mechanism of oxidation of Cr(II) ions by salicylaldehyde
Effect of reversible reaction in the rate-determining step

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The true reaction order determined from the initial rates by the differential method with respect to the concentration of Cr(II) ions is lower than the reaction order determined by both the integral and the differential methods with respect to time. Cr(III) ions retard the redox reaction of Cr(II) ions with salicylaldehyde and the rate of increase of Cr(III) products corresponds to the rate of decrease of Cr(II) ions. The effect of a reversible reaction in the rate-determining step of this non-complementary redox reaction is discussed.

Although the basic information provided by the rate law is the composition of the activated complexes [1], it is more frequent to use this information for determination of the reaction mechanism. The form of the rate law indicates a model of the mechanism conformable to experimental data but it is questionable whether another reaction mechanism may exist, which is no less in accordance with the rate law. If the total stoichiometry of the reaction differs from the composition of the activated complex, then, after the rate-determining step, subsequent steps involving one or more intermediates must be considered.

The most popular way of determining the reaction order, *i.e.* the integral method, is generally known to be not quite reliable [2]. This method characterizes the way how the concentration of the reactants or products changes with time. The most important quantities, the initial rate and the true reaction order, *i.e.* the reaction order with respect to the concentration of reactants, can be obtained by the differential method determining the course of changes of the reaction rates with the concentration of reactants. By measurements of the initial rates at various initial concentrations of the reactants we may avoid possible complications caused by the interference of the products and determine the true reaction order with respect to the concentration of reactants. The second procedure using the differential method consists in measurements of the reaction rates at various times, corresponding to various concentrations of the reactants. Thus obtained reaction order is called the order with respect to time and it corresponds to the reaction order determined by the integral method.

For a given reaction, these two reaction orders need not be the same [2]. When the true reaction order n_c is smaller than the order n_t with respect to time, it means that an intermediate or a reaction product causes the inhibition. On the contrary, when n_t is smaller than n_c, the reaction is called autocatalytic.

Kinetic studies of the reduction of benzaldehyde by Cr(II) ions revealed the retardation effect of Cr(III) ions [3]. The effect of Cr(III) ions on the kinetics of the redox reaction of Cr(II) ions with salicyladehyde that is even more pronounced is the subject of this work.

Experimental

The used chemicals and experimental details were described elsewhere [4]. The kinetics of the reduction of salicylaldehyde by Cr(II) ions was examined polarographically, the time dependence of the limiting diffusion anodic current of Cr(II) ions was recorded at a constant potential. The wave of Cr(II) ions was found to have a diffusion character in the used medium (water—methanol—perchloric acid). Of all the reactants and products only Cr(II) ions increased the current at the selected potential. In the absence of salicylaldehyde the wave height of Cr(II) ions did not change with time. No reaction between salicylaldehyde and methanol was observed. A sufficient excess of the oxidant (ca. 100-fold) was always used and the time dependences for the reaction of the pseudo--first order

$$\log \frac{i_0}{i} = f(t) \qquad (1)$$

and for the reaction of the pseudo-second order

$$\frac{1}{i} = f(t), \qquad (2)$$

were plotted in diagrams. Symbols i_0 and i stand for the limiting diffusion current of Cr(II) ions at the beginning of the reaction and at the time t respectively. The rate constants were evaluated from the initial rates

$$k_{obs} = \left| \left(-\frac{d\,[Cr(II)]}{dt} \right)_{t=0} \frac{1}{[Cr(II)]_0} \right| = \left| \left(-\frac{di}{dt} \right)_{t=0} \frac{1}{i_0} \right|. \qquad (3)$$

The kinetic data obtained polarographically were checked by spectrophotometry

$$k_{obs} = \left(\frac{dA}{dt} \right)_{t=0} \frac{1}{A_\infty - A_0}, \qquad (4)$$

where A_0 and A_∞ are the respective absorbances at the beginning and after the reaction. The rate constants represent the mean values from at least three measurements. The accuracy of the determination of k_{obs} was $\pm 6\%$.

Results and discussion

The integral method used for determining the reaction order of the redox reaction of Cr(II) with salicylaldehyde in a sufficient excess (Figs. 1 and 2) would indicate that it is the reaction of the second order with respect to the concentration of Cr(II) ions. However, the reaction order determined by the differential method from initial concentrations with respect to the Cr(II) concentration is equal to one since the data in Table 1 show a linear relationship
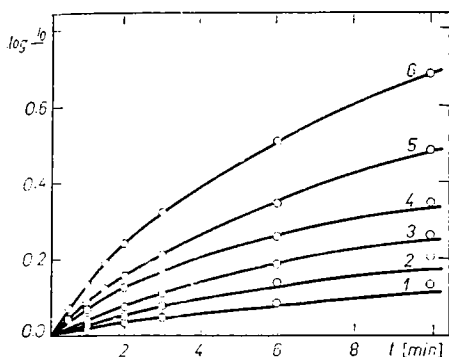
$$\log v_0 = \log k + n \log c_0 \qquad (5)$$

Fig. 1. Graphical time dependence of the pseudo-first order reaction of Cr(II) ions with salicylaldehyde.
50% Methanol, 0.5 M-HClO$_4$, 2 × 10^{-3} M-Cr(II), $t = 25°$C.
Concentration of salicylaldehyde:
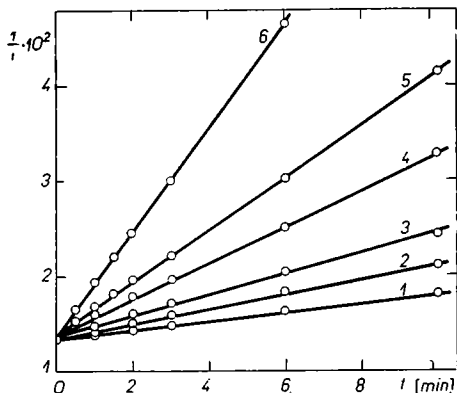1. 0.05 M; 2. 0.08 M; 3. 0.1 M; 4. 0.15 M; 5. 0.2 M; 6. 0.3 M.

Fig. 2. Time dependence of the reciprocal value of the limiting diffusion current of Cr(II) ions.
For the conditions see Fig. 1.

with the slope $n = 1.05$. The differentially determined order with respect to the concentration of salicylaldehyde is also 1 (Table 2). From the time course of the concentration of Cr(II) ions (2 × 10^{-3} M-Cr(II)$_0$) in the presence of 0.3 M salicylaldehyde, the slope $n_t = 1.81$ of the linear relationship $\log v = f(\log c)$ was determined by the differential method.

The rate of increase of the Cr(III) products in the redox reaction of Cr(II) ions with salicylaldehyde was examined also spectrophotometrically at wavelengths 411 and 580 nm, corresponding to the absorption maxima of Cr(III) complexes. The values of $k_{obs} = 1.36 \times 10^{-3}$ s^{-1} and 1.28×10^{-3} s^{-1} calculated from eqn (4) are in very good agreement with those obtained by polarography under the same con-

Table 1

Change of the kinetic parameters with the concentration of Cr(II) ions

i_0 (Scale lines)	$v_0 = \left(\dfrac{di}{dt}\right)_{t=0}$	k_{obs} [s^{-1}]
20	5.02 × 10^{-2}	2.51 × 10^{-3}
40	9.31 × 10^{-2}	2.32 × 10^{-3}
67	1.76 × 10^{-1}	2.62 × 10^{-3}
71	1.66 × 10^{-1}	2.35 × 10^{-3}
80	2.07 × 10^{-1}	2.60 × 10^{-3}
110	2.93 × 10^{-1}	2.66 × 10^{-3}

50% Methanol, 0.5 M-HClO$_4$, 0.15 M salicylaldehyde, $t = 25°$C.

Table 2

Change of the kinetic parameters with the concentration of salicylaldehyde

[Salicylaldehyde]	$v_0 = \left(\dfrac{\mathrm{d}i}{\mathrm{d}t}\right)_{t=0}$	k_{obs} [s^{-1}]
0.05	4.67×10^{-2}	6.23×10^{-4}
0.08	7.33×10^{-2}	9.77×10^{-4}
0.10	1.18×10^{-1}	1.57×10^{-3}
0.15	1.84×10^{-1}	2.45×10^{-3}
0.20	2.43×10^{-1}	3.24×10^{-3}
0.30	3.66×10^{-1}	4.88×10^{-3}

50% Methanol, 0.5 M-HClO$_4$, 2×10^{-3} M-Cr(II) (75 scale lines), $t = 25°C$.

ditions (48% methanol, 0.1 M salicylaldehyde, and 0.5 M-HClO$_4$ at 25°C). The rate of increase of the Cr(III) complexes also corresponded to the rate of decrease of Cr(II) ions.

The reaction order with respect to time is in fact higher than the order with respect to the Cr(II) concentration; this means that an intermediate or a product of the redox reaction exerts the inhibitory effect. The decrease of the initial rate by the effect of hexaaquochromium(III) ions is proved by the values of $k_{obs} = 1.35 \times 10^{-3}$, 6.21×10^{-4}, and 4.76×10^{-4} s^{-1} found in the presence of 2×10^{-4}, 5×10^{-2}, and 10^{-1} M-Cr(III) ions respectively, in 40% methanol, 0.1 M salicylaldehyde, and 0.5 M-HClO$_4$ at 25°C. The observed decrease cannot be explained by the change of the ionic strength of the solution since such a change from 0.5 to 1.0 brings about a decrease in the rate constant by 10% only. The decrease of the initial rate occurs also when a reaction mixture resulting from a preceding reaction of 3×10^{-3} M-Cr(II) with 0.1 M salicylaldehyde in 40% methanol and 0.5 M-HClO$_4$ is regarded as the initial state. On the other hand, a repeated addition of Cr(II) ions into the reaction mixture with the excess $(10^{-2}-10^{-1}$ M) of Cr(III) ions does not bring about any further retardation of the reaction. The retardation is obviously not caused by other products but Cr(III) ions.

The first step of the reaction scheme of the reduction of benzaldehyde by Cr(II) ions [3] is

$$\mathrm{Cr(II)} + \text{oxidant} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \mathrm{Cr(III)} + \mathrm{R\cdot} \qquad (A)$$
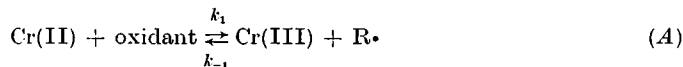
where the formed radical R$\cdot$ can react quickly (rate constant k_2) with another Cr(II) ion. The application of this scheme to the reduction of salicylaldehyde using the stationary-state principle for R$\cdot$ leads to the following rate equation

$$-\frac{\mathrm{d}\,[\mathrm{Cr(II)}]}{\mathrm{d}t} = \frac{2k_1\,k_2\,[\mathrm{Cr(II)}]^2\,[\text{ald}]}{k_{-1}\,[\mathrm{Cr(III)}] + k_2\,[\mathrm{Cr(II)}]} \qquad (6)$$

at the constant concentration of hydrogen ions ([ald] stands for salicylaldehyde).

This rate equation is in conformity with experimental data. The true reaction order defined by eqn (6) with respect to Cr(II) is one, provided the initial Cr(III) concentration is zero. Eqn (6) also expresses the retardation effect of Cr(III) ions as

well as the change of the reaction order with respect to the Cr(II) concentration at a great initial excess of Cr(III) ions.

If the second term in the denominator of eqn (6) can be omitted in comparison with the term k_{-1} [Cr(III)], which is possible at high Cr(III) and low Cr(II) concentrations, the dependence $1/[Cr(II)] = f(t)$ will become linear with the slope $2k_1 k_2$ [ald]$/k_{-1}$ [Cr(III)]. When 0.1 M-Cr(III)$_0$, 2×10^{-3} M-Cr(II)$_0$, and 0.1 M salicylaldehyde were used in 40% methanol and 0.5 M-HClO$_4$, the dependence $1/i = f(t)$ was satisfactorily linear. The slope was calculated after one half-life when the ratio [Cr(III)]/[Cr(II)] became greater than 100. Since the concentrations of both Cr(III) and aldehyde practically do not vary during the reaction (Cr(III) increases by 1% at the half-life) and $2k_1$ is in fact identical with k_{obs} determined from the initial rates in the absence of Cr(III) ions, we obtain the ratio $k_2/k_{-1} = 17$. When the ratio [Cr(III)]/[Cr(II)] is equal to 17, the two terms in the denominator of eqn (6) have a mutually equal weight. In the course of the reaction the contribution of the second term decreases and can be eliminated by a substantial increase of the initial concentration of Cr(III) ions. For benzaldehyde, the ratio k_2/k_{-1} is 36 [3]. The retardation of the reaction by the effect of the same amount of Cr(III) ions is more marked with salicylaldehyde, which is reflected in the lower value of the ratio k_2/k_{-1}.

The integration of eqn (6) yields a rather unusual [5] relationship

$$\frac{k_{-1}([Cr^{II}]_0 + [Cr^{III}]_0)}{k_2 - k_{-1}\left(1 + \dfrac{[Cr^{II}]_0 + [Cr^{III}]_0}{2\,[ald]_0 - [Cr^{II}]_0}\right)} \frac{1}{[Cr^{II}]} - \ln \frac{[Cr^{II}]}{2\,[ald]} =$$

$$= \frac{k_2(2\,[ald]_0 - [Cr^{II}]_0)}{k_2 - k_{-1}\left(1 + \dfrac{[Cr^{II}]_0 + [Cr^{III}]_0}{2\,[ald]_0 - [Cr^{II}]_0}\right)} k_1 t + \text{int. const.} \qquad (7)$$

Providing that $[Cr^{III}]_0 = 0$ and the 100-fold excess of salicylaldehyde towards $[Cr^{II}]_0$ is maintained, eqn (7) can be simplified and rearranged into

$$\frac{[Cr^{II}]_0}{[Cr^{II}]} - \left(\frac{k_2}{k_{-1}} - 1\right) \ln \frac{[Cr^{II}]}{2\,[ald]} = \frac{2k_1 k_2\,[ald]}{k_{-1}} t + \text{int. const.} \qquad (8)$$

The validity of this relationship is verified by inserting various values of the ratio k_2/k_{-1} into equation. For the properly selected k_2/k_{-1} value, the time dependence of the left side of eqn (8) is linear. The method gives satisfactory results as long as the initial concentrations of reactants are not too different. In the studied case where $[ald]_0 = 0.2$ M and $[Cr(II)]_0 = 2 \times 10^{-3}$ M, this procedure is not too sensitive to the changes in k_2/k_{-1}. The time dependence of the left side of eqn (8) is satisfactorily linear for the ratio $k_2/k_{-1} = 17$ obtained from the slope of the tangent lines to the curves of the time dependence of the Cr(II) concentration as well as for the ratio $k_2/k_{-1} = 1$, corresponding also to the situation illustrated in Fig. 2.

From the slope of dependence (8) the value $2k_1 = 3.33 \times 10^{-3}$ s^{-1} was determined for $k_2/k_{-1} = 1$ and the value $2k_1 = 1.36 \times 10^{-3}$ s^{-1} for $k_2/k_{-1} = 17$. The experimental value obtained by the differential method under the same conditions is $k_{obs} = 3.24 \times 10^{-3}$ s^{-1}. The rate constants obtained by the differential method have to be regarded more reliable in this case. However, from any used method, merely values of k_1 and the ratio k_2/k_{-1} can be obtained.

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Translated by F. Kopecký