

KINETICS OF REDUCTION OF BENZALDEHYDE BY Cr(II) IONS

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The kinetics of reduction of benzaldehyde by Cr(II) ions in water-methanol-perchloric acid and water-acetic acid-perchloric acid systems was studied. The reaction is first order with respect to both benzaldehyde and Cr(II) concentration. The hexaaquochromium(III) ions retard the reaction rate. The effect of hydrogen ions depends on the solvent used, as does the stoichiometry of the reaction. The activation parameters were obtained by Eyring's equation. A reaction mechanism is suggested in which the formation of α -hydroxybenzyl radical and hexaaquochromium(III) ion is the rate determining step. The α -hydroxybenzylchromium(III) intermediate, formed by the association of the radical with a further chromium(II) ion, is considered the direct precursor of benzyl alcohol and bimolecular products.

When benzaldehyde is reduced by Cr(II) ions, the reaction products are benzyl alcohol and bimolecular products such as hydrobenzoin and its derivatives in various yields, depending on the solvent, the hydrogen ion concentration and the presence of various ions¹⁻³. Recently⁴, in a study on the reduction of benzaldehyde by Cr(II) ions in ethanol, there appeared the possibility of an intermediate containing a C—Cr bond. It was assumed that the particles that actually react are a protonated hydrate of benzaldehyde and its dimer⁴. A detailed kinetic study of the reduction of benzaldehyde by Cr(II), aimed at the formation and degradation of the organometallic intermediate, in water-methanol-perchloric acid and water-acetic acid-perchloric acid media, appeared to be useful, and is the subject of this work.

EXPERIMENTAL

Chemicals. Benzaldehyde, analytical grade (Lachema), was purified before use by chromatography on a Al_2O_3 column and subsequently distilled under nitrogen atmosphere. The middle fraction, b.p. 179°—180°C, was collected and stored under nitrogen atmosphere. The Cr(II) solution was prepared by dissolving metal chromium (99.999%, Koch-Light) in perchloric acid of a given concentration (usually 0.5—1M) under nitrogen atmosphere. The chromium was activated in 6M-HCl before dissolving. Atmospheric oxygen was carefully removed from all solutions that came into contact with Cr(II) by passing oxygen-free nitrogen. Nitrogen was purified by passing through solutions of Cr(II) ions, prepared by reducing a 1M solution of chromic sulphate with zinc amalgam. Methanol and acetic acid were rectified before use. Perchloric acid (Apolda), sodium perchlorate (Fluka), sodium acetate (Lachema), chromium (III) perchlorate (Serva International) were all analytical grade chemicals and used without any further purification.

Stoichiometry. An excess of $\text{Cr}(\text{ClO}_4)_2$ was allowed to react with benzaldehyde. After 4 days of reaction at room temperature the unreacted $\text{Cr}(\text{ClO}_4)_2$ was determined polarographically from the limiting diffusion current of $\text{Cr}(\text{II})$. The following procedure was adopted as control: after 4 days an excess of FeCl_3 was added to the reaction mixture. The FeCl_2 formed quantitatively and was determined by titration with $\text{Na}_2\text{Cr}_2\text{O}_7$ in acidic medium. The equivalence point was determined potentiometrically. It was found that 0.619 mol of $\text{Cr}(\text{II})$ were consumed per 0.3 mol of benzaldehyde in a 50% (v/v) water-acetic acid mixture. On back-titration 0.616 mol of $\text{Cr}(\text{II})$ were consumed per 0.3 mol of benzaldehyde, in the same medium. When 50% (v/v) water-methanol medium was used, out of the total 0.49 mol of $\text{Cr}(\text{II})$, 0.17 mol remained unreacted with 0.3 mol of benzaldehyde in 4 days. These facts lead to the conclusion that the stoichiometry 1 : 1 in methanol differs from the stoichiometry 2 : 1 in acetic acid and indicates that the reaction products are different in both media.

Analysis of reaction products. A reaction system of the initial concentrations 0.9M- $\text{Cr}(\text{II})$, 0.38M benzaldehyde, 0.9M- HClO_4 in 47% acetic acid, was allowed to react for one week at room temperature. No precipitation was observed. The reaction mixture was then extracted with three 50 ml portions of chloroform. The extract was washed with water, dried with dehydrated Na_2SO_4 , and was allowed to evaporate freely. About 0.5 ml of slightly yellow liquid was thus obtained and was analysed by gas-chromatography on a Fractovap model G1, Carlo Erba, with a Speedomax recorder. The glass column was 2 m long, 2 mm in diameter, and filled with 2% XE-60 on Chromosorb W (60–80 mesh). Temperature of the column was 109.5°C. The chromatogram showed two peaks in the ratio of about 1 : 10. Co-injection proved that the first peak is due to unreacted benzaldehyde while the second is that of benzyl alcohol. The position of both peaks was in accordance with that of standard solutions of benzyl alcohol and benzaldehyde.

In a system of initial concentrations 0.9M- $\text{Cr}(\text{II})$, 0.77M benzaldehyde, 0.9M- HClO_4 in 46% methanol, white needle-like crystals formed which could be separated by filtration. After washing with methanol, 110 mg of the substance, melting point 86.5–88°C, was obtained. Quantitative isolation of this product from the reaction mixture was not attempted. The substance was compared with white crystals prepared by reducing benzoin with LiAlH_4 in dioxane and benzene. The substance prepared by the reduction of benzoin was re-crystallized from methanol; its melting point was 86–88°C.

Inorganic products of the reaction were isolated by chromatography on Dowex 50 W-X 2 (200–400 mesh), H^+ form. On extraction with chloroform, the aqueous phase of the reaction mixture was separated; part of it was poured into an ion-exchanging column 8 cm long, 1 cm in diameter. For eluting the $\text{Cr}(\text{III})$ complexes 2M- HClO_4 was necessary. The shape of the spectrum and the value of the half-wave potential proved that hexaaquochromium(III) is the only final product of the redox reaction.

Spectrophotometric and polarographic measurements. Spectrophotometric measurements were performed on a Zeiss Specord UV-VIS Spectrophotometer (Jena). The reaction proceeded in 3 cm thick quartz cells closed hermetically, at 20°C. The disappearance of the organometallic intermediate was followed under conditions when the redox reaction was practically finished at temperatures of 20, 30 and 40°C. This reaction, a consecutive one from the point of view of the rate determining step, was performed under nitrogen atmosphere. It was followed by absorption measurements at 410 and 572 nm where the hexaaquochromium(III) has a maximum with $\epsilon_{410} = 15.6 \text{ l mol}^{-1} \text{ cm}^{-1}$ and $\epsilon_{572} = 13.5 \text{ l mol}^{-1} \text{ cm}^{-1}$. A correction for the absorption of $\text{Cr}(\text{II})$, with $\epsilon_{572} = 1.4 \text{ l mol}^{-1} \text{ cm}^{-1}$ was used. It was assumed that no other species absorbs around 572 nm, and the contribution of absorbance of the intermediate was calculated at 410 nm wavelength. The rate constants of the consecutive reaction were obtained by plotting $\log A_{\text{intermed}}$ vs t . Polarographic measurements were performed on a LP-55 polarograph

with an electronic compensation recorder, EZ-2 (Laboratorní přístroje). The Kalousek polarographic vessel, modified for water temperature control, was used as a reaction vessel. A mercury dropping electrode with drop-time 3.3 s, flow rate 2.24 mg/s at 64 cm height of mercury column was used as the indicator electrode. Saturated calomel electrode (s.c.e.) was used as reference electrode. Nitrogen atmosphere was carefully maintained during all polarographic measurements.

Kinetics of reduction of benzaldehyde by Cr(II) was followed by recording the limiting diffusion anodic current of Cr(II) at a constant potential of +0.1 V (s.c.e.) as a function of time. It was found that the Cr(II) wave is a diffusion wave in both media. At the potential of +0.1 V (s.c.e.), of all substances taking part in the reaction, only Cr(II) ions increase the current. If benzaldehyde is not present the height of the Cr(II) wave does not change with time in any media used in the experiments and, similarly, no reaction of benzaldehyde with acetic acid or methanol was observed. In all experiments a sufficient excess of benzaldehyde (100 fold on the average) was used. The rate constants of the redox reaction were obtained from the initial rates, using a differential method, according to the expression:

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

where i_0 is the limiting diffusion current of Cr(II) at time $t = 0$. The values of rate constants given are the averages of at least three measurements. The accuracy of determining k_{obsd} was within $\pm 6\%$. Graphic evaluation of rate constants from the integrated form of the rate law was less accurate because of deviations induced by the retarding effect of Cr(III) formed by the reaction.

RESULTS

The spectrophotometric record of the reaction of benzaldehyde with Cr(II) in 50% aqueous solution of acetic acid in 1M-HClO₄ indicates a slow increase of absorbance in the visible region of the spectrum (Fig. 1). The resulting spectrum has maxima at 410 and 572 nm. Extinction coefficient values ($\epsilon_{410} \sim 15$, $\epsilon_{572} \sim 14$) indicate that the resulting reaction product is a Cr(III) complex which contains only Cr—O bonds, probably a hexaquo chromium(III) ion. The rate of increase of this complex corresponds to the rate of decrease of Cr(II), as was found by polarography under the same conditions. On the other hand, the reaction in 50% aqueous methanol in 1M-HClO₄, under otherwise identical conditions with those of acetic acid, differs markedly both in the shape of its spectrum and in the time dependence of absorbance (Fig. 2). In the initial phase of the reaction in methanol the colour of the reaction mixture is yellow-orange and only gradually changes to the blue-violet colour of hexaquo chromium(III). Absorbance at 572 nm increases less rapidly in methanol than in acetic acid, while in the range of 380–415 nm the increase of absorbance is more pronounced and proves the presence of a Cr(III) complex with minimum value of $\epsilon_{410} \sim 200 \text{ l mol}^{-1} \text{ cm}^{-1}$. As absorbance at 410 nm reaches the maximum value, when the actual redox reaction of Cr(II) with benzaldehyde is practically complete as all the Cr(II) ions are exhausted, it slowly decreases again. This corresponds to the decomposition of an unstable Cr(III) complex. The rate constant of this decomposition was calculated: $k'_{\text{obsd}} = 6.5 \cdot 10^{-5} \text{ s}^{-1}$ in 0.5M benzaldehyde, 1M-HClO₄, at 40°C. This reaction is not catalysed by Cr(II), as proved by equal value of a rate constant k'_{obsd} for initial concentrations of Cr(II) 10^{-2} M , $2 \cdot 10^{-2} \text{ M}$ and $4 \cdot 10^{-2} \text{ M}$. Activation parameters for this reaction are: $\Delta E^\ddagger = 12.3 \pm 0.7 \text{ kcal mol}^{-1}$ and $\Delta S^\ddagger = -40 \pm 2 \text{ cal deg}^{-1} \text{ mol}^{-1}$. The resulting absorption spectrum in methanol resembles the spectrum of hexaquo chromium(III).

Kinetics of the redox reaction of Cr(II) with benzaldehyde. The rate of disappearance of Cr(II) in sufficient excess of benzaldehyde, followed polarographically, shows the reaction to be first order with respect to Cr(II). With increasing time, however, the reaction rate decreases, as compared to first order kinetics, in both media, which indicates that the actual order in Cr(II) ions differs from the reaction order obtained from concentrations *vs* time plots. It was found that the reaction rate decreases even further in the presence of chromium(III) salts where the departure from first order kinetics is still more pronounced (Table I).

The reaction order with respect to the concentration of Cr(II) was determined, in view of this effect, by a differential method using initial concentrations. The slope of the plot $\log v_0 = f(\log [\text{Cr(II)}_0])$ is 1.06 and the slope of the plot $\log v_0 = f(\log [\text{benzaldehyde}])$ is 1.10 in acetic acid. This proves that the reaction is first order with respect to both reactants. A similar result was also found in methanol where for 0.5, 1, 1.5 and 2M benzaldehyde values of k_{obsd} are $4.49 \cdot 10^{-4} \text{ s}^{-1}$, $9.57 \cdot 10^{-4} \text{ s}^{-1}$, $1.5 \cdot 10^{-3} \text{ s}^{-1}$ and $2.01 \cdot 10^{-3} \text{ s}^{-1}$ respectively for 1.26M-HClO₄ at a temperature of 36°C. The character of the dependence of $k_{\text{obsd}} = f[\text{HClO}_4]$ differs in the two media. In the case of acetic acid, the initial reaction rate reaches minimum for concentration range 0.2–0.3M-HClO₄ (Fig. 3). The simplest function to describe this dependence is of the type (1):

$$k_{\text{obsd}} = a + b \cdot [\text{H}^+] + \frac{c}{[\text{H}^+]}. \quad (1)$$

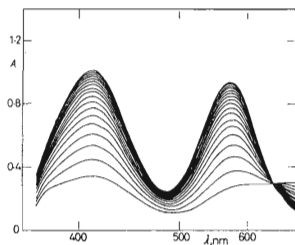


FIG. 1

Spectrophotometric Observation of the Reaction of Benzaldehyde with Cr(II) in 50% Aqueous Solution of Acetic Acid

$2 \cdot 10^{-2}$ M-Cr(II)₀, 0.5M benzaldehyde, 1M-HClO₄, temperature 20°C, recorded after 492 s.

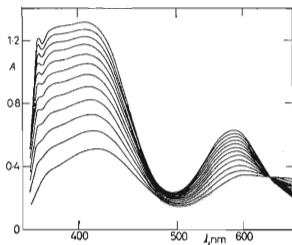


FIG. 2

Spectrophotometric Observation of the Reaction of Benzaldehyde with Cr(II) in 50% Aqueous Solution of Methanol

Conditions as in Fig. 1.

Numerically (using the least square method) it was impossible to straighten the curve accurately enough. This may have been due to lower accuracy in determining the

TABLE I

The Effect of Cr^{3+} Ions on the Initial Reaction Rate v_0 of the Reduction of Benzaldehyde with Cr(II) Ions at 25°C

[B] ^a	[Cr ³⁺]	$v_0 \cdot 10^6, \text{l}^{-1} \text{mol s}^{-1}$
50% acetic acid ^b		
1	$1.3 \cdot 10^{-3}$	5.4
1	$7.7 \cdot 10^{-3}$	4.5
1	$3.3 \cdot 10^{-2}$	3.5
50% methanol ^c		
1.5	$5.0 \cdot 10^{-4}$	7.5
1.5	$5.0 \cdot 10^{-3}$	7.2
1.5	$5.0 \cdot 10^{-2}$	4.1
1.5	$1.0 \cdot 10^{-1}$	3.1
1.5	$1.5 \cdot 10^{-1}$	2.3

^a Benzaldehyde; ^b $7.7 \cdot 10^{-3} \text{M-Cr(II)}$, 1M-HClO₄, ^c $5.2 \cdot 10^{-3} \text{M-Cr(II)}$, 2M-HClO₄.

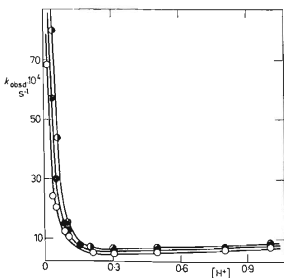


FIG. 3

Dependence of the Rate Constant on HClO₄ Concentration in 50% Acetic Acid at 15°C (○) 25°C (●), 40°C (●)

$3.8 \cdot 10^{-3} \text{M-Cr(II)}$, 1M benzaldehyde.

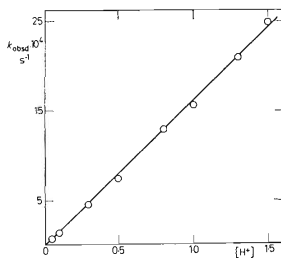


FIG. 4

Dependence of the Rate Constant on HClO₄ Concentration in 50% Methanol at 36°C $7.9 \cdot 10^{-3} \text{M-Cr(II)}$, 2M benzaldehyde.

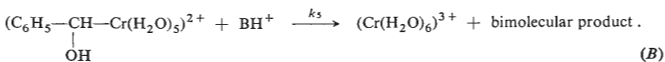
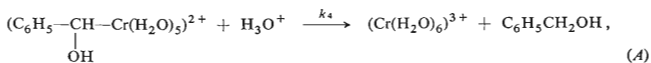
rate constants by the differential method in the case of a faster reaction, *i.e.* in the case of low HClO_4 concentrations in acetic acid. In the case of methanolic media, the initial reaction rate is proportional to perchloric acid concentration. The linear plot $k_{\text{obsd}} = f[\text{HClO}_4]$ intersects the origin of the coordinates (Fig. 4).

Studying the effect of ionic strength on the reaction rate in 50% acetic acid, we found that the rate constant $k_{\text{obsd}} = 1.14 \cdot 10^{-3} \text{ s}^{-1}$ was independent of ionic strength in the interval 0.1–1 in 0.1M- HClO_4 at 25°C. The rate constant does not depend on acetic acid concentration from a 50% to a 70% solution in 1M- HClO_4 . It was found, in accordance with the observed dependence of k_{obsd} on hydrogen ion concentration in acetic acid, that with decreasing dielectric permeability of the medium (increasing acetic acid concentration) the rate constant increases parabolically in 0.06M- HClO_4 . A wider range of acetic acid concentrations cannot be used because of the limited solubility of benzaldehyde and the conditions for the diffuse character of the Cr(II) current. The possible participation of acetate ions in the rate determining step was excluded as sodium acetate does not induce any change in the rate constant $k_{\text{obsd}} = 6.29 \cdot 10^{-4} \text{ s}^{-1}$ in 1M- HClO_4 , 1M benzaldehyde at 25°C, for the concentration range of acetate ions from 0–3 $\cdot 10^{-2}$ M in 50% methanol, nor in the constant $k_{\text{obsd}} = 7.2 \cdot 10^{-4} \text{ s}^{-1}$ in 50% acetic acid the under same conditions. Increase in temperature has very little effect on the reaction rate. The activation parameters, calculated from Eyring's expression, are: $\Delta E^\ddagger = 1.4 \pm 0.3 \text{ kcal mol}^{-1}$, $\Delta S^\ddagger = -70 \pm 4 \text{ cal deg}^{-1} \text{ mol}^{-1}$ in 50% acetic acid and $\Delta E^\ddagger = 1.8 \pm 0.3 \text{ kcal mol}^{-1}$, $\Delta S^\ddagger = -68 \pm 3 \text{ cal deg}^{-1} \text{ mol}^{-1}$ in 50% methanol, ionic strength being 1.

DISCUSSION

Our results show that the product of the redox reaction of Cr(II) with benzaldehyde is benzyl alcohol in acetic acid medium while in methanol medium bimolecular products are formed. The similar values of rate constants of the redox reaction in 1M- HClO_4 , of activation parameters, the same reaction orders, a similar effect of Cr(III) on the reaction rate, all argue in favour of an identical rate determining step in the mechanism of reduction of benzaldehyde by Cr(II) in sufficiently acidic media in both solvents. The yellow-orange colouring of the reaction system in methanol seems to indicate the formation of a complex of Cr(III) with an organic ligand, including a C—Cr bond. Its value of $\epsilon_{410} \sim 200 \text{ l mol}^{-1} \text{ cm}^{-1}$ is decidedly higher than in Cr(III) complexes with an oxygen bond^{5,6}, but lower than in alkyl(en)-chromium(III) complexes⁷, or in the pentaquo(diethylether)chromium(III) ion⁸ where for the range 390–400 nm, $\epsilon \sim 360\text{--}335 \text{ l mol}^{-1} \text{ cm}^{-1}$ is found, and which also contain the C—Cr bond. The value of $\epsilon_{410} \sim 200 \text{ l mol}^{-1} \text{ cm}^{-1}$ estimated by us is the minimum one, as either aquation or any other reaction of the intermediate causes decrease in absorbance. In acetic acid medium the concentration of Cr(II) decreases at a rate which roughly equals the rate of hexaquo chromium(III) forma-

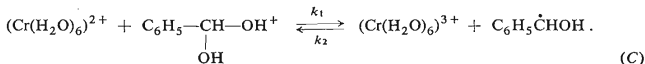
tion. Since the kinetic results of the reaction in both media are similar, the formation of an organometallic compound as an intermediate can be expected in acetic acid medium as well. In this case, however, the decomposition of the intermediate is many times faster than in methanol. That is probably caused by acetate ions which also have a catalytic effect on the rate of protolysis of benzylchromium(III) and other alkylchromium(III) complexes^{7,9}. Acetic acid has a roughly 100 fold greater effect than other acids (hydrochloric, perchloric, sulphuric) of the same concentration. It is assumed that the rate determining protolysis of the complex, rendered easier by the lowered charge of the complex⁹, follows immediately after a fast reversible reaction in which substitution of a molecule of water by an anion of the acid takes place. We therefore presume that benzyl alcohol is mainly formed by acetolysis of α -hydroxybenzylchromium(III) ion which is identical with the intermediate containing the C—Cr bond. The formation of bimolecular products (first probably hydrobenzoin or isohydrobenzoin, later methyl- or dimethyl-derivatives of hydrobenzoin⁴) takes place in excess of benzaldehyde, when the protolysis of α -hydroxybenzylchromium(III) is sufficiently slow, that is in water methanolic media. The identical values of pseudo-first-order rate constants for the decomposition of the intermediate, with different initial concentrations of Cr(II) if the reaction rate is determined by protolysis of the intermediate, exclude a catalytic effect of Cr(II) ions. Anet¹⁰ observed the catalysis by Cr(II) in the aquation of benzylchromium(III) in presence of halide ions. The activation parameters for aquation of benzylchromium(III) were⁹: $\Delta H^\ddagger = 16.2$ kcal mol⁻¹ and $\Delta S^\ddagger = -13.9$ cal deg⁻¹ mol⁻¹. Similar values were found for other organochromium(III) intermediates as well⁸. However, our results are significantly different. We therefore assume that the bimolecular products are formed by a redox reaction of α -hydroxybenzylchromium(III) with benzaldehyde. Reactions leading to the final reaction products are probably



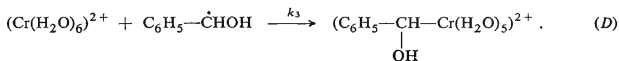
Analogous equations were formulated for the formation of toluene and dibenzyl from benzylchromium(III)⁹, and form one of the alternatives suggested by Davis and Bigelow⁴ in a study of the reduction effect of Cr(II) on water-ethanolic solutions of benzaldehyde. Our results prove that the α -hydroxybenzylchromium(III) ion is the common direct precursor of the organic products of this reaction.

The effect of HClO₄ concentration on the reaction rate both in methanol and in acetic acid at [HClO₄] > 0.2M, indicates that the actual reacting particle is a proton-

ated form of benzaldehyde, more likely of its hydrate (as can be seen from the fact that k_0 , the intercept in linear plots of k_{obsd} vs HClO_4 concentration, which corresponds to a reaction path of a nonprotonated form of benzaldehyde, equals zero). The actual redox reaction is preceded by a fast reversible reaction characterized by the protonation constant K_p . The mechanism of reduction of benzaldehyde by Cr(II), agreeing with experimental results, includes the formation of α -hydroxybenzyl radical and hexaaquochromium(III) ion as the rate determining step:



Since in perchloric acid media hexaaquochromium(III) products are formed, while in hydrochloric acid CrCl^{2+} forms⁴, we can assume that actually a bridged activated complex is formed. An oxygen containing group, originating from benzaldehyde, plays the role of the bridge ligand. The reaction characterized by rate constant k_2 is assumed on the grounds of the dependence on hexaaquochromium(III) concentration. It is possible to expect that the association of the formed radical with a further Cr(II) ion will be fast and will lead to the formation of a C—Cr bond:



The rate constant of association, $k_a = 4 \cdot 10^7 \text{ l mol}^{-1} \text{ s}^{-1}$, is already known for the association of alkyl radicals with $\text{Cr}(\text{en})_2^{2+}$ ions⁷. Expressions (A) and (B) indicate the transformation of the intermediate. The proportion of the final reaction products depends on the ratio of rate constants k_4 and k_5 of these reactions.

We may use the term $k_{\text{obsd}} \sim c \cdot [\text{H}^+]^{-1}$ to describe the dependence of the rate constant on HClO_4 concentration in water-acetic acid medium for $[\text{HClO}_4] < 0.2\text{M}$. This term may mean that the protons are produced prior to the rate determining step. These protons originate again from benzaldehyde, as the hydrolysis of $(\text{Cr}(\text{H}_2\text{O})_6)^{2+}$ can be neglected¹¹. Though the extent of ionisation of benzaldehyde in water-acetic acid media is not known, and doubtless very small, the mono- and di-anion of a hydrated form of benzaldehyde may be important from a kinetic point of view¹². (Constants b and c in Eq. (1) represent the product of rate constants and equilibrium constants of the respective active forms of benzaldehyde.) The absence of a term expressing inverse dependence of the rate constant on HClO_4 concentration in methanol reflects the different protolytic characteristics of benzaldehyde in the solvents used.

The reaction is first order with respect to Cr(II) concentration and benzaldehyde concentration in both media. The plot $\log i_0/i = f(t)$ is, even in sufficient excess

of benzaldehyde, linear only in the early phases of the reaction, and the direction of the curvature indicates that a back reaction is becoming important. Chromium(III) retards the redox reaction, and when the initial excess of Cr^{3+} over Cr(II) is more than 30fold the plot $1/i = f(t)$ is satisfactorily linear. This points toward a change of reaction order in Cr(II) from 1 to 2 and to an inverse dependence of reaction rate on Cr^{3+} concentration. This effect was not studied by Davis and Bigelow⁴, but leads to a modified mechanism.

Equation (2), obtained experimentally, is valid on condition that the initial concentration of Cr^{3+} approaches zero and the

$$\text{initial rate} = - \frac{d[\text{Cr(II)}]_0}{dt} = k_{\text{obsd}} \cdot [\text{Cr}^{2+}]_0, \quad (2)$$

excess of benzaldehyde is sufficient. Using the stationary-state principle for the α -hydroxybenzyl radical, the mechanism proposed gives

$$- \frac{d[\text{Cr}^{2+}]}{dt} = \frac{2k_1k_3K_p[\text{Cr}^{2+}]^2 [\text{B}] [\text{H}^+]}{k_2[\text{Cr}^{3+}] + k_3[\text{Cr}^{2+}]}, \quad (3)$$

where [B] stands for the analytical concentration of benzaldehyde. The concentration of Cr^{2+} represents, in our case, the overall concentration of Cr(II). If the initial concentration of Cr^{3+} is zero then it follows from equation (3) that

$$\text{initial rate} = \frac{d[\text{Cr}^{2+}]_0}{dt} = 2k_1K_p[\text{Cr}^{2+}] [\text{B}] [\text{H}^+]. \quad (4)$$

Comparing this with experimental expression (2) we obtain equation (5)

$$k_{\text{obsd}} = 2k_1K_p[\text{B}] [\text{H}^+], \quad (5)$$

which is in accordance with the relationship for the concentration of benzaldehyde and hydrogen ions (in acetic acid medium from 0.2M- HClO_4 onward, when the protonated form of benzaldehyde reacts) and with the reaction order found with respect to Cr(II) concentration. Under conditions when $k_2[\text{Cr}^{3+}]$ is considerably larger than $k_3[\text{Cr}^{2+}]$ we obtain, from equation (3),

$$- \frac{d[\text{Cr}^{2+}]}{dt} = \frac{k_1k_3K_p[\text{Cr}^{2+}]^2 [\text{B}] [\text{H}^+]}{k_2[\text{Cr}^{3+}]}, \quad (6)$$

which accords with the observed dependence and describes the change of reaction order with respect to Cr(II) concentration in a great excess of Cr^{3+} . The ratio k_3/k_2 can be estimated using Eq. (6), with the help of equation (5): $k_3/k_2 = 36$. The association of the radical with the Cr(II) ions, which are labile in substitution, involves only a very low activation energy because of the quintet character of the high-spin Cr(II) ions in solution, and therefore a higher value of rate constant k_3 may be expected.

The plot $\log i_0/i = f(t)$, under otherwise identical conditions, deviates from a straight line in acetic acid more and earlier than in methanol. This supports the suggestion that the rate of formation of hexaquo chromium(III) is slower in methanol than in acetic acid. Degradation of α -hydroxybenzylchromium(III) in methanol is sufficiently slow (in contrary to acetic acid medium) and therefore the Cr^{3+} ions, formed on the reaction of the intermediate, no longer retard the redox reaction of benzaldehyde with Cr(II) ions.

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