

## CATALYZED OXIDATION OF HYDROQUINONE WITH HYDROGEN PEROXIDE

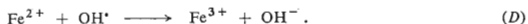
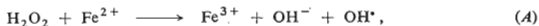
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Oxidation of hydroquinone with hydrogen peroxide, catalyzed by ferrous ions bound in complex compounds with different stability and kinetic behaviour, was studied. Kinetic course of the reaction under various conditions has been explained by assuming a reactive ternary complex formed by the catalyst and the two reacting components.

Oxidation of organic compounds with hydrogen peroxide catalyzed by ferrous ions, the so-called Fenton reaction<sup>1</sup>, has been used for a long time and in a fairly wide extent for preparative purposes. In spite of this an interpretation of the reaction mechanism which could explain all the observed effects is still lacking. Neither the original Fenton's explanation based on the assumption of a complex formed by the catalyzing ion and the oxidized substance<sup>2</sup> nor the conception of Murmery<sup>3</sup> that it is the oxidation by active oxygen, formed in the reaction of hydrogen peroxide with the peroxo complex of the catalyst, complied with the results of later kinetic studies and were replaced by the still adopted idea of radical mechanism. The radical mechanism<sup>4-6</sup> is based on the assumption that either hydroxyl or O<sub>2</sub>H· radicals formed in the reactions (A) or (B) and (C) respectively, react with the substrate under the formation of the corresponding free radicals



These radicals react either in a chain mechanism<sup>8</sup> or, if the termination reactions prevail, in a non-chain mechanism. A concurrent reaction of OH· radicals with Fe<sup>2+</sup> ions (D) has been also considered<sup>8</sup>. Decomposition of peroxide, catalyzed by ferrous and ferric ions and oxidation of organic substances by Fenton's reagent, particularly the kinetics and thermodynamics of these reactions, were studied by a number of authors<sup>7-17</sup>. All of them consider the radical mechanism, however, they differ in their concepts of the course of partial reactions. So *e.g.* Uri<sup>9</sup> classified the compounds that are oxidized with peroxide under the catalytic effect of Fe<sup>2+</sup> and Fe<sup>3+</sup> ions into three groups: 1) Substances oxidized by hydrogen peroxide in the presence of ferrous and ferric salts but neither by peroxide nor by ferric salt alone. 2) Substances oxidized by hydrogen peroxide in the presence of ferrous and ferric salts and oxidized by ferric salts alone, however, not oxidized by peroxide alone. 3) Compounds oxidized by hydrogen peroxide in the presence of ferrous salts,

but neither by peroxide alone nor by peroxide in the presence of ferric salts. For each of these groups Uri assumes a different mechanism and different radical intermediates. Although the radical mechanism of Fenton's reaction corresponds principally to the kinetic data and no serious objections can be raised even from the point of view of thermodynamics of the reaction, radical mechanism need not be, according to Sigel<sup>15-17</sup>, the only possible interpretation of catalytic oxidation by peroxide.

Kinetic data and thermodynamic considerations seem not to provide sufficient informations allowing unambiguously either to confirm or to refuse a particular mechanism. The decisive factor for the interpretation of the mechanism will be probably the elucidation of the role of catalyst. For this reason an attempt was made in the present study to gain new data on the catalytic action of  $\text{Fe}^{2+}$  and  $\text{Fe}^{3+}$  ions, both as such, *i.e.* only hydrated, and bound in complex compounds of various stability and various kinetic characteristics on one of the oxidation reactions of hydrogen peroxide. Hydroquinone was chosen as a substrate for this study. According to Uri's classification<sup>9</sup> hydroquinone belongs to the second group, since it is oxidized by peroxide in the presence of  $\text{Fe}^{2+}$  and  $\text{Fe}^{3+}$  ions and also by ferric salts, but not by hydrogen peroxide alone.

## EXPERIMENTAL

Hydrogen peroxide (30%) was a Lachema ultra pure reagent and was not stabilized. *p*-Benzoquinone<sup>18</sup> and 2,5-dihydroxybenzoquinone<sup>19</sup> were prepared as described. All other chemicals were of reagent grade purity and some of them were further purified: Buffer solutions were freed from heavy metals by extraction with dithizone. Hydroquinone was purified by repeated crystallization. The content of traces of heavy metals in the chemicals used was determined by emission spectrography on a Zeiss Q 24 apparatus.

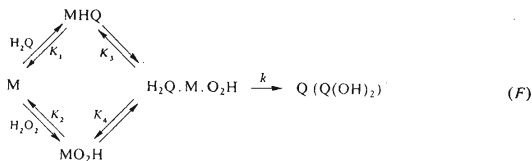
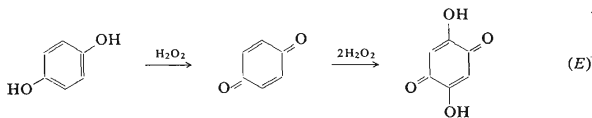
The course of the reaction was followed spectrophotometrically on a Specol (Carl Zeiss, Jena) colorimeter in the visible region and on a Unicam SP 800 spectrophotometer in the UV region. In both cases the reaction proceeded in a thermostatted c. 100 ml vessel, connected with the instrument cell by a PVC tube. Stirring of the solution and its circulation between the reaction vessel and the cell was ensured by a teflon worm, placed in the vessel. This arrangement was described earlier<sup>20</sup>. The change of hydroquinone concentration in a mixtures containing also other components, absorbing in the UV region was measured against a reference solution of the same composition, but containing no hydroquinone. In all other cases water served as reference solution. Absorption spectra in both visible and ultraviolet regions were recorded on Unicam SP 800 spectrometer.

## RESULTS AND DISCUSSION

### *Reaction Course*

Oxidation of hydroquinone with hydrogen peroxide proceeds at a measurable rate only in the presence of ferrous, ferric or cupric ions, giving yellow-orange ( $\text{pH} < 4.0$ ) or red ( $\text{pH} > 4.6$ ) colouration which during the reaction changes to brown and finally

to almost black. After some hours a dark brown precipitate separates, especially from more concentrated solutions. The yellow-orange colour, appearing immediately after mixing the components at  $\text{pH} > 4.0$ , changes sharply into red upon alkalization and *vice versa*, the red changes to yellow upon acidification. In alkaline medium oxidation is accomplished already by air oxygen. In a strongly acid medium, as *e.g.* in  $1\text{M-H}_2\text{SO}_4$  a greenish-yellow colour appears gradually which changes to orange and to brown only after some hours or sooner upon heating. The reaction course also depends on the composition of the buffers used. In Britton–Robinson and citrate buffers which contain substances masking the catalyst, the reaction does not proceed, however it does proceed in veronal or acetate buffer. Reaction catalyzed by  $\text{Cu}^{2+}$  proceeds even in pyridine buffer in spite of the fact that pyridine forms complexes with copper. Spectrophotometric investigation of the course of the reaction of hydroquinone ( $\text{H}_2\text{Q}$ ) with peroxide which was carried out in acetate or veronal buffer in the  $\text{pH}$  range  $3.5-5.5$  and with concentration of components ranging  $5 \cdot 10^{-3}$  to  $2 \cdot 10^{-2}\text{M}$ , the ratio of the initial components  $\text{H}_2\text{Q}/\text{H}_2\text{O}_2$  varying from  $1:10$  to  $10:1$ , revealed always a distinct decrease of the hydroquinone absorption maximum at  $288\text{ nm}$  and formation of a not too distinct maximum at  $450\text{ nm}$ , followed



later on by the formation of a further maximum at  $340\text{ nm}$ . Eventually a continuous absorption resulted which, however, changed a little for some more weeks. The final reaction product has a continuous spectrum at  $250-550\text{ nm}$  which, however, varies according to reaction conditions. The reaction course can best be illustrated by scheme (E): Hydroquinone ( $\text{H}_2\text{Q}$ ) is oxidized with hydrogen peroxide to quinone (Q) which further reacts for form dihydroxy-*p*-benzoquinone ( $\text{Q}(\text{OH})_2$ ), yielding with the unreacted hydroquinone quinhydrone. This last compound polymerizes slowly to humine substances. As the first step dihydroxybenzoquinone could be identified spectrophotometrically (at  $450\text{ nm}$ ). Quinone (absorption maximum at  $429\text{ nm}$ ) was not detected, but its formation as intermediate is to be presumed, since

both quinone and hydroquinone yield dihydroxybenzoquinone<sup>19</sup> in reaction with hydrogen peroxide. In view of the fact that the molar extinction coefficient of quinone is rather small within the whole range of wave-lengths used, differing only very little from that of the other components of the system whose concentrations in the mixture are, however, by order of magnitude greater than the possible concentration of quinone as intermediate, it even cannot be expected that it could be detected spectrophotometrically. The formation of quinone is also supported by the fact that the dependence of the initial rate of hydroquinone loss  $-(d[H_2Q]/dt)_0$ , on the initial concentration of components at a constant sum  $[H_2Q]_0 + [H_2O_2]_0 = \text{const.}$  shows a maximum at  $[H_2Q]_0/[H_2O_2]_0 = 1 : 1$ , whereas the same dependence of the initial rate of dihydroxybenzoquinone formation shows this maximum at the ratio 1 : 3 (Fig. 1). The ratio of the rate constants of the considered partial reactions can be estimated also from the data of Strelcova and Petraš<sup>22</sup> who give the values of the rate constant of the reaction of hydroquinone with hydrogen peroxide, catalyzed by  $Cu^{2+}$  ions  $k_1 = 0.88 \text{ mol}^{-1} \text{ l min}^{-1}$  and of the reaction of quinone with hydrogen peroxide under the same conditions  $k_2 = 5.46 \cdot 10^2 \text{ mol}^{-1} \text{ l min}^{-1}$ . Obviously the first reaction is the rate determining step, however, the reaction of quinone to dihydroxybenzoquinone is also not so fast, as compared with the first process, as to make possible the assumption that  $-(d[Q]/dt) = 0$  during the whole course of the reaction. The absorption maximum at 340 nm can be explained by the formation of quinhydrone, since a similar absorption curve is displayed also by the product of the reaction of dihydroxybenzoquinone with hydroquinone. Continuous absorption and the separation of scarcely soluble products from the solution correspond to the formation of humine substances. Reaction of phenols with peroxide was studied from the point of view of the formed products by Musso<sup>21</sup>.

#### *Kinetics of Reaction Catalyzed by Ferrous Ions*

The reaction course was followed spectrophotometrically at the wave length corresponding to the maximum hydroquinone absorption (288 nm), *i.e.* following  $-d[H_2Q]/dt$  as well as at 450 nm, corresponding to maximum absorption of the first spectrophotometrically detectable product, dihydroxybenzoquinone, *i.e.*, by following  $+d[Q(OH)_2]/dt$ . From the time course of the reaction found at the mentioned wave lengths it is evident that  $-(d[H_2Q]/dt) \neq +(d[Q(OH)_2]/dt)$ . Bearing in mind that we have a system of consecutive reactions where dihydroxybenzoquinone is neither the first intermediate nor the final reaction product and that hydroquinone shows at 288 nm a distinct and sharp absorption maximum with a relatively high extinction coefficient ( $\epsilon = 2.5 \cdot 10^2 \text{ mol}^{-1} \cdot \text{l} \cdot \text{cm}^{-1}$ ) with the concentration dependence linear over the whole concentration range studied, we have followed the reaction course only in terms of the hydroquinone loss, *i.e.* according to  $-(d[H_2Q]/dt)$ .

From the dependence of the initial rate of hydroquinone loss on the concentration of both reacting components and of ferrous ions it was found, using the method

of van'tHoff<sup>25</sup> that the initial reaction rate is approximately proportional to the first power of the concentrations of hydroquinone, hydrogen peroxide and of ferrous ions and consequently that  $-(d[\text{H}_2\text{Q}]/dt)_0 = k[\text{H}_2\text{Q}]_0 [\text{H}_2\text{O}_2]_0 [\text{Fe}^{2+}]_0$ . With a higher excess of one or other of the reaction components the reaction rate increase with increasing concentration of the particular component is greater than it would correspond to the mentioned relation. As can be seen from Fig. 1, initial rate of hydroquinone loss and of dihydroxybenzoquinone formation exhibit maxima at different stoichiometric ratios. When the loss of hydroquinone was followed under the condition that  $[\text{H}_2\text{Q}]_0 = [\text{H}_2\text{O}_2]_0$ , it was established that the reaction course can be described by the above mentioned kinetic equation up to 15% of hydroquinone consumed. In these experiments the concentration of the reacting components was  $[\text{H}_2\text{Q}]_0 = [\text{H}_2\text{O}_2]_0 = 1 \cdot 10^{-3}\text{M}$  and that of ferrous ions was varied between  $10^{-5}$  and  $10^{-7}\text{M}$ . The work was carried out in acetate buffer pH 5 at 25, 30 and 35°C. With respect to the fact that the overall concentration of catalyzing ions, without considering valence changes, does not change during the reaction and that  $[\text{H}_2\text{Q}]_0 = [\text{H}_2\text{O}_2]_0$ , the values of rate constants were calculated from the relation

$$k = x/ta(a - x), \quad (1)$$

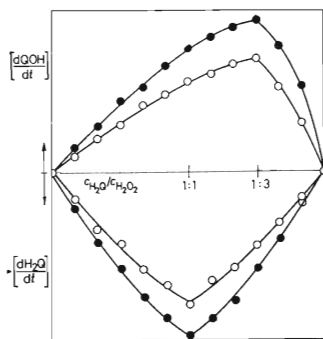


FIG. 1

Dependence of the Initial Reaction Rate on the Ratio  $c_{\text{H}_2\text{Q}} : c_{\text{H}_2\text{O}_2}$  at Constant Sum

$c_{\text{H}_2\text{Q}} + c_{\text{H}_2\text{O}_2}$   
 ○  $[\text{Fe}^{2+}] = 6 \cdot 10^{-6}\text{M}$ , ●  $[\text{Fe}^{2+}] = 1 \cdot 10^{-5}\text{M}$ .

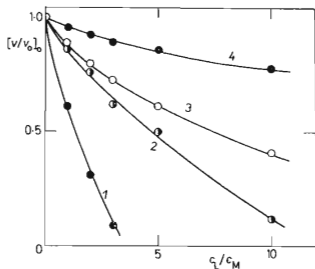


FIG. 2

Dependence of  $(v/v_0)_0$  on  $c_L/c_M$

1 Citric acid, 2 oxalic acid, 3 sulphosalicylic acid, 4 fluoride.

where  $a = [\text{H}_2\text{Q}]_0 = [\text{H}_2\text{O}_2]_0$ , and  $x$  is the hydroquinone loss. The dependence of rate constants on  $[\text{Fe}^{2+}]_0$  was expressed in the form of regression equation  $v = k_0 + k_1[\text{Fe}^{2+}]_0 + k_2[\text{Fe}^{2+}]_0^2$ , where the coefficients  $k_0$  and  $k_2$  proved statistically insignificant on the level  $\alpha = 0.95$ . This means that the reaction does not proceed at a measurable rate at zero concentration of the catalyst and that the dependence of the initial reaction rate on the concentration of iron ions for  $[\text{Fe}^{2+}]_0 = 10^{-5}$  to  $10^{-7}\text{M}$  is linear. The dependence on  $[\text{Fe}^{3+}]_0$  is not linear and the results are rather poorly reproducible. A possible explanation is that at pH 5 ferric salts, contrary to ferrous salts, are hydrolyzed to a high degree. Petrašev and Strelcova<sup>22</sup>, when studying the reaction catalyzed by cupric ions in the medium of weakly acid pyridine buffer, found a linear dependence of the initial reaction rate on  $[\text{Cu}^{2+}]_0$ .

The dependence of the initial reaction rate on the concentration of ferrous ions for  $[\text{H}_2\text{Q}]_0 = [\text{H}_2\text{O}_2]_0 = 1 \cdot 10^{-3}\text{M}$  was determined at 25, 30 and 35°C. The found dependence of the rate constant on  $[\text{Fe}^{2+}]_0$  was: at 25°C  $k = 4.18 \cdot 10^4[\text{Fe}^{2+}]_0$ , at 30°C  $k = 5.76 \cdot 10^4[\text{Fe}^{2+}]_0$  and at 35°C  $k = 6.77 \cdot 10^4[\text{Fe}^{2+}]_0$ . The calculated value of the apparent activation energy was  $E_a = 20.7 \text{ kcal/mol}$ .

#### Kinetics of Reaction Catalyzed by Complex Ions

Further experiments were performed to study the effect of various substances which form with the catalyzing ferrous, ferric and cupric ions complexes of different stability and with different kinetic behaviour, on the kinetics of the catalyzed reaction. The following effects were observed: a great excess of any complexing agent leads to a complete stop of the reaction in any phase of its course. Addition of the complexing agent in concentration, comparable with that of the catalyzing ions causes either a decrease of the reaction rate without changing the shape of the kinetic curve or changes the kinetic course which is reflected by the formation of a delay on the

TABLE I

Values of the Real Concentration of the Catalyzing Ion  $\text{M}(\text{Cu}^{2+})$  and of the Concentration Calculated from the Rate of Oxidation of Hydroquinone by Peroxide  $[\text{M}_v]$

$c_M = 1 \cdot 10^{-4}\text{M}$ , complex forming reagent EDTA, pH 5, acetate buffer.

$\frac{c_L}{c_M}$	[M]	$[\text{M}_v]$	$A = \frac{[\text{M}]}{c_M}$	$B = \left(\frac{v}{v_0}\right)_0$	$\frac{B}{A}$
0.0	$1.0 \cdot 10^{-4}$	$1.0 \cdot 10^{-4}$	1.00	1.00	1.00
0.5	$5.0 \cdot 10^{-5}$	$5.7 \cdot 10^{-5}$	$5.0 \cdot 10^{-1}$	$5.7 \cdot 10^{-1}$	1.14
1.0	$2.5 \cdot 10^{-8}$	$2.5 \cdot 10^{-6}$	$2.5 \cdot 10^{-3}$	$2.5 \cdot 10^{-1}$	$1.00 \cdot 10^2$
1.1	$1.6 \cdot 10^{-11}$	$2.0 \cdot 10^{-5}$	$1.6 \cdot 10^{-7}$	$2.0 \cdot 10^{-1}$	$1.25 \cdot 10^6$

kinetic curve, giving it an S-shape. It was found that this different effect of complexing agent is connected with the kinetic behaviour of the formed complex. Complexing agents which form labile complexes cause a decrease of the reaction rate without changing the shape of the kinetic curve. This effect was found *e.g.* with fluorides, salicylic acid, sulphosalicylic acid, oxalic acid and citric acid and  $\text{Fe}^{2+}$  or  $\text{Fe}^{3+}$  as catalyzing ions and with all the investigated complexing reagents and  $\text{Cu}^{2+}$  as catalyzing ion. Contrary to this, reagents forming inert complexes with the catalyzing ions cause delays on the kinetic curve, *e.g.*, addition of sodium salt of ethylenediamine tetraacetic acid (EDTA) or *o*-phenanthroline, both of them forming inert complexes with ferrous and ferric ions, causes a delay on the kinetic curve. If EDTA or *o*-phenanthroline is added to the reaction system containing cupric ions as catalyst, only a decrease of the reaction rate takes place without any change of the shape of the kinetic curve, since both reagents form labile complexes with  $\text{Cu}^{2+}$ . Investigation of the effect of reagents forming inert complexes with catalyzing ions is made difficult by the poor reproducibility of the results as well as by the fact that the reaction course depends on the sequence of the components added to the system and on the time intervals between the additions of the particular components. Therefore, in further experiments only the effect of reagents, forming labile complexes, was followed.

The effect of the complexing agent on the rate of catalyzed reaction is characterized by the quantity  $(v/v_0)_0$ , *i.e.* by the ratio of the initial rate of reaction catalyzed by a certain amount of the catalyst upon addition of the complex forming reagent, ( $v$ ), to that of the reaction catalyzed by the same amount of the catalyst, however, without addition of the complex forming reagent, ( $v_0$ ). The ratio  $(v/v_0)_0$  can attain values from zero to unity; it equals zero, when the reaction does not proceed at all, *i.e.* when it is stopped by excess of complexing reagent and it equals unity, when the addition of the reagent has no influence on the effect of metal ions. Fig. 2 shows the effect of some complex forming reagents on the oxidation of hydroquinone catalyzed by  $\text{Fe}^{2+}$  ions. It is evident that  $(v/v_0)_0$  decreases with increasing ratio  $c_L/c_M$ , however, even at  $c_L \gg c_M$  the reaction rate is considerably higher than it would correspond to the concentration of free metal catalyst ion. Even at  $c_L \gg c_M$  further additions of the complex forming reagent result in a decrease of the reaction rate, in spite of the fact that the ratio of concentration of free and complex bound ions does not change appreciably any more. Effect of various complex-forming reagents at a constant, addition, expressed as  $c_L/c_M$ , is essentially given by the value of the stability constant of the formed complex, although some reagents, forming less stable complexes (*e.g.* citric and oxalic acids) display a greater influence than reagents with more stable complexes with the catalyzing metal (*e.g.* sulphosalicylic acid). The probable cause might be that at pH 5, at which our experiments were carried out, dissociation of the complexes of the catalyst with different complex forming reagents is affected to various extent by the actual concentration of  $\text{H}^+$  ions.

As for the initial rate of reaction, catalyzed by a complex bound ion, a great difference was found between the free ion concentration, calculated assuming an equilibrium between the free and the complex bound ion and the concentration corresponding to the found initial reaction rate. In Table I the ratio  $A$ , i.e. the ratio of the concentration of free metal ion  $[M]$  to the total analytical concentration of metal ion,  $c_M$ , calculated from the value of the stability constant  $K$  for a given  $c_L/c_M$ , is compared with the experimentally found value of  $B = (v/v_0)_0$ . If the initial reaction rate depended only on  $[M]$ , the ratio  $B/A$  should be constant and equal to unity. This, however, is not the case and the found value  $B/A \approx 10^6$  cannot be explained by experimental errors.

The value of  $(v/v_0)_0$  depends also on the ratio of the sum of initial concentrations of the components, or on the ratio of the sum of initial concentrations of the components to the initial concentration of the catalyzing ion ( $[H_2Q]_0 + [H_2O_2]_0$ )/ $c_M$ , as it is evident from Table II. The table shows the dependence of  $(v/v_0)_0$  on the excess of components, expressed by the term  $([H_2Q]_0 + [H_2O_2]_0)/c_M$  at constant sum  $[H_2Q]_0 + [H_2O_2]_0$ , but at varying ratio  $[H_2Q]_0 : [H_2O_2]_0$ . It is evident that the value of  $(v/v_0)_0$ , particularly at  $[H_2Q]_0 = [H_2O_2]_0$  depends very distinctly on the ratio  $([H_2Q] + [H_2O_2])/[M]$ , the value of  $(v/v_0)_0$  decreasing with decreasing value of the ratio. This means that the effect of the complexing agent on the reaction rate is the lower the higher is the excess of both or at least of one of the two reaction components in the mixture.

### Reaction Mechanism

The accepted mechanism of reactions of organic compounds with Fenton's reagent is based on the concept of the formation of  $OH^*$  radicals reacting with the oxidized substance. These reactions are denoted in the introductory part of the present paper as (A), (C) and (D). Reaction (C), taken into account also in the catalytic decomposition of  $H_2O_2$  and resulting in the release of  $O_2$  is not considered here, because no formation of  $O_2$  has been observed in the oxidation with Fenton's reagent. If we start from equation (A) as the rate determining step and provided the subsequent radical reactions are fast, we can employ the assumption of a steady state ( $d[OH^*]/dt = 0$ ). Then the kinetic equation has the form

$$v = - \frac{d[H_2Q]}{dt} = \frac{k_1[Fe^{2+}][H_2O_2][H_2Q]}{k_3[H_2Q] + k_4[Fe^{2+}]} \quad (2)$$

This relation can be applied to the observed course for the conditions  $[H_2Q]_0 = [H_2O_2]_0$ , only if  $k_3[H_2Q] + k_4[Fe^{2+}]$  is constant. Since this prerequisite is entirely competent for the beginning of the reaction, no objections can be raised against the radical mechanism from the kinetic point of view. Besides, this mechanism



was derived by Haber and coworkers<sup>4-6</sup> from kinetic data. However, if we take  $v = -(d[\text{H}_2\text{Q}]/dt)_0 = k_A[\text{Fe}^{2+}]_0$  or  $k'_A[\text{Cu}^{2+}]_0$ , where  $k_A = k[\text{H}_2\text{Q}]_0 [\text{H}_2\text{O}_2]_0$ , then in the case of validity of the radical mechanism this dependence should be valid even if the catalyst concentration is decreased by addition of the complexing reagent. Thus it should hold that  $[\text{M}]/c_M = (v/v_0)_0$ . However, in Table I we find discrepancies, especially for  $c_L/c_M > 1$ , that cannot be explained by radical mechanism. Even the possible objection that the complex bound catalyst produces hydroxyl radicals at a lower rate, does not hold out; this explanation is in contradiction with the experimentally found dependence of  $(v/v_0)_0$  on the value of  $([\text{H}_2\text{Q}]_0 + [\text{H}_2\text{O}_2]_0)/c_M$ , shown in Table II. Neither the Baxendale's conception<sup>10</sup> of "Katalasestoß" can be applied in our case, as a similar effect is observed with reagents where  $\text{p}K_{\text{Fe}^{2+}} : \text{p}K_{\text{Fe}^{3+}} \geq 1$ ,  $\text{p}K_{\text{Fe}^{n+}}$  being the stability constant of the complex of the reagent with an n-valent ion. Of course, all these facts present such severe disagreement of the radical mechanism with the experimentally found results that its correctness appears doubtful. Here it should be mentioned that the above results are neither the first nor the single ones that are at variance with the radical mechanism; doubts as to its applicability for the explanation of catalyzed oxidation by peroxide have been expressed earlier<sup>15</sup>.

Another possible mechanism, presumed *e.g.* in enzymatically catalyzed reactions, is the formation of a ternary complex which by decomposition yields the first intermediate<sup>26</sup>. This mechanism is illustrated by Scheme (F), where  $K_1$  to  $K_4$  are the equilibrium constants of the formed binary, resp. the ternary complex. The formation of a complex compound of the catalyst, *i.e.* of  $\text{Fe}^{2+}$ ,  $\text{Fe}^{3+}$  and  $\text{Cu}^{2+}$  with hydro-

TABLE II

Change of the Value  $(v/v_0)_0$  in Dependence on  $[\text{H}_2\text{Q}]_0 + [\text{H}_2\text{O}_2]_0/c_M$  for  $[\text{H}_2\text{Q}]_0 = [\text{H}_2\text{O}_2]_0$  and for a Five-Fold Excess of One of the Components

Complex-forming reagent citric acid,  $c_L/c_M = 1.00$ .

Catalyst	$\frac{[\text{H}_2\text{Q}]_0 + [\text{H}_2\text{O}_2]_0}{c_M}$	$(v/v_0)_0$		
		$[\text{H}_2\text{Q}]_0 = [\text{H}_2\text{O}_2]_0$	$[\text{H}_2\text{Q}]_0 = 5[\text{H}_2\text{O}_2]_0$	$5[\text{H}_2\text{Q}]_0 = [\text{H}_2\text{O}_2]_0$
$\text{Fe}^{2+}$	$5 \cdot 10^4$	0.80	0.51	0.50
	$2 \cdot 10^4$	0.71	0.50	0.49
	$5 \cdot 10^3$	0.63	0.50	0.48
	$8 \cdot 10^2$	0.54	0.49	0.47
$\text{Cu}^{2+}$	$2 \cdot 10^4$	0.66	0.60	0.52
	$5 \cdot 10^3$	0.62	0.58	0.50

quinone (M.HQ) is quite doubtless. Also the peroxocomplexes, whose formation is also considered, have been described<sup>23</sup>. Further, the formation of the ternary complex (HQ.M.O<sub>2</sub>H) may be expected, at least with a certain probability. The assumption that the first intermediate of the reaction, be it quinone (Q) or dihydroxybenzoquinone (Q(OH)<sub>2</sub>), is formed by decomposition of the ternary complex enables us to interpret all the found experimental data. According to this mechanism the catalyst is the component necessary for the course of the reaction. This, of course could be explained even by the radical mechanism. The over-all reaction is 2-nd order. The added complex-forming reagent has actually only a relatively small effect on the reaction rate, particularly if both components, hydroquinone and hydrogen peroxide, are present in great excess, since it represents only a third competitive complexing agent which, even if forming rather stable complex compounds (*e.g.* EDTA with Cu<sup>2+</sup>) play no role in the excess of components which themselves form complexes with the catalyzing cations. An important fact that can be explained by the new suggested mechanism is that the decrease of the initial reaction rate, caused by the alien complex forming reagent, decreases with the increasing excess of the components and attains a minimum at  $[\text{H}_2\text{Q}]_0 = [\text{H}_2\text{O}_2]_0$  for constant sum  $[\text{H}_2\text{Q}]_0 + [\text{H}_2\text{O}_2]_0 = \text{const}$ . The competitive effect of the third complex-forming reagent is the stronger, the less is the excess of at least one of the components. The new mechanism is also able to explain why an even greater than stoichiometric addition of the complexing reagent only slows-down the reaction and also explains better than the radical mechanism does why different metal ions have different effects on the oxidation of various organic substances by peroxide. This kind of "selectivity" of the catalyst in oxidation by hydrogen peroxide has also found application in analytical chemistry<sup>24</sup>. There the condition is that a ternary complex be formed and consequently the "selectivity" of the catalyst is conditioned by the possibility of the formation of a ternary complex and by its stability. The suggested mechanism can further elucidate the dependence of the reaction rate on pH in the way that H<sup>+</sup> ions enhance the dissociation of binary complexes, thus hindering the formation of ternary complex. Also the course of the dependence of the reaction rate on the concentration of the catalyst agrees with the suggested mechanism. For the comparable stability constants of binary complexes of the catalyst with both components it holds that

$$-(d[\text{H}_2\text{Q}]/dt)_0 = k([\text{HQM}] [\text{H}_2\text{O}_2] + [\text{MO}_2\text{H}] [\text{H}_2\text{Q}]), \quad (3)$$

$$-(d[\text{H}_2\text{Q}]/dt)_0 = k'([\text{H}_2\text{Q}]_0 [\text{H}_2\text{O}_2]_0 [\text{M}]_0)/([\text{H}_2\text{Q}]_0 + [\text{H}_2\text{O}_2]_0), \quad (4)$$

where  $k$  is the real rate constant and  $k'$  is a constant including in addition to the rate constant also the stability constant of both binary and of the ternary complex. Linear dependence  $-(d[\text{H}_2\text{Q}]/dt)_0$  on  $c_M$  for low concentrations of catalyzing ions has been experimentally proved at least for Fe<sup>2+</sup> and Cu<sup>2+</sup> and the nonlinear dependence

on  $\text{Fe}^{3+}$  could be explained by assuming hydrolysis. Moreover,  $\text{Fe}^{3+}$  reacts directly with hydroquinone under the formation of quinone<sup>13</sup> which rather complicates the whole reaction. It has been further found that the expression

$$[\text{H}_2\text{Q}]_0 [\text{H}_2\text{O}_2]_0 / ([\text{H}_2\text{Q}]_0 + [\text{H}_2\text{O}_2]_0) = c_A c_B / (c_A + c_B) \quad (5)$$

from the kinetic equation (4) has for  $c_A + c_B = c = \text{const.}$  an extremum in the concentration range  $c_A = 0, c_B = c$  to  $c_A = c, c_B = 0$ . Analysis of the extremum of the expression  $y = c_A c_B / (c_A + c_B)$ , where  $c_A + c_B = c = \text{const.}$  showed that the extremum is given by the condition  $y' = c - 2c_A = 0$ , i.e. if  $c_A = c_B$  and that it is a maximum, since  $y'' = -2 < 0$ . This maximum can be really seen in Fig. 1.

Formation of the ternary complex according to Scheme (F) is considered by Laidler<sup>26</sup> also for enzymatically catalyzed reactions. His solution is only a result of an extended validity of the equation of Michaelis and Menten<sup>27</sup> and is not limited to the initial reaction rate. In our case, i.e. considering Scheme (F) and using the same notation of stability constants, we obtain the relation

$$-\frac{d[\text{H}_2\text{Q}]}{dt} = k \frac{K_1 K_3 [\text{Fe}^{2+}]_0 [\text{H}_2\text{Q}] [\text{H}_2\text{O}_2]}{1 + \{K_1 [\text{H}_2\text{O}_2] + K_2 [\text{H}_2\text{Q}] + K_1 K_3 [\text{H}_2\text{Q}] [\text{H}_2\text{O}_2]\}} \quad (6)$$

Under the justified assumption that  $\{K_1 [\text{H}_2\text{O}_2] + K_2 [\text{H}_2\text{Q}] + K_1 K_3 [\text{H}_2\text{Q}] [\text{H}_2\text{O}_2]\} \ll 1$ , this relation attains the form  $-(d[\text{H}_2\text{Q}]/dt)_0 = k^* [\text{Fe}^{2+}]_0 [\text{H}_2\text{Q}]_0 [\text{H}_2\text{O}_2]_0$ , where  $k^* = k K_1 K_3$ , which has been experimentally proved.

Other alternatives of possible mechanisms were also considered, e.g. the formation of a complex of hydroquinone with the catalyst and its reaction with  $\text{H}_2\text{O}_2$  according to the original Fenton's concept, and the formation of quinone or dihydroxybenzoquinone by interaction of binary complexes of the catalyst with the components. Provided that the Fenton's mechanism were valid the stability constant of the complex of the catalyzing ion with phenol could be expressed by a simple relation from the known values of the stability constant of the metal ion with the complexing reagent and it could be then calculated from the experimental data. However, the calculated values differ for various ratios  $c_1/c_M$  and for various complex forming reagents as much as by several orders of magnitude. Consequently, neither this mechanism can be accepted without serious objections.

Another proposed mechanism, the interaction of two binary complexes, would imply that the kinetic equation required for  $-(d[\text{H}_2\text{Q}]/dt)_0$  to be dependent on  $[\text{Fe}^{2+}]^2$ , which means that the graphical plot of this dependence would be a curve, strongly convex towards the  $[\text{Fe}^{2+}]$  axis. The really found dependence was a linear one and its slope was determined by the method of least squares and its linearity was tested on the level  $\alpha = 0.95$  for the whole studied  $[\text{Fe}^{2+}]$  concentration range. Therefore, even this mechanism can be taken as less probable than the concept of the ternary complex.

From the above considerations it results that the assumption of the formation of a ternary complex of both components with the catalyst and of the formation of the first intermediate by decomposition of this complex provides explanation not only of the kinetic reaction course, but also of the data which were in disagreement with the Fenton's mechanism<sup>1</sup>, the radical mechanism of Haber and Weiss<sup>6</sup> and also with the conception that the first product is formed by interaction of binary complexes of the catalyst with the components. The presented mechanism can thus be taken as the most plausible of all the hitherto suggested mechanisms of hydroquinone oxidation by hydrogen peroxide.

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