OXIDATION OF METOL, RESORCINOL AND PYROCATECHOL WITH HYDROGEN PEROXIDE, CATALYZED BY Cu^{2+} IONS

K.Eckschlager, I.Horsák and J.Vepřek-Šiška

Institute of Inorganic Chemistry,
Czechoslovak Academy of Sciences, 250 68 Prague - Řež

Oxidation of metol, resorcinol and pyrocatechol with hydrogen peroxide, catalyzed by Cu^{2+} ions, both as such and bound in a complex with nitrilotriacetic acid and ethylenediaminetetraacetic acid, has been investigated. The kinetic course of the reaction under various conditions is interpreted in terms of a reactive intermediary ternary complex of the catalyst with both reacting components. The experimentally determined initial reaction rates were compared with the values computed for the assumed reaction mechanism and a fairly good agreement was found.

Our previous work[1] dealt with the oxidation of hydroquinone with hydrogen peroxide, catalyzed by Fe^{2+}, Fe^{3+} and Cu^{2+} ions[2]. We compared different reaction mechanisms with the experimental results and we found the concept of a ternary complex hydroquinone–catalyst–peroxide to be the most satisfactory. This complex decomposes to quinone which is hydroxylated to dihydroxy-*p*-benzoquinone reacting eventually to humic substances. The concept of the formation of a ternary complex has been employed when interpreting some enzymatically catalyzed reactions[3]. Recently, this mechanism has also been considered in the interpretation of reactions catalyzed by metallic ions[1,4,5].

In the present work we have investigated the oxidation of some further aromatic compounds, *viz* resorcinol, pyrocatechol and metol with hydrogen peroxide in order to find out whether the mechanism of hydroquinone oxidation with hydrogen peroxide is of a wider validity. At the same time, we have attempted to compare experimental results with the values calculated for the assumed mechanism.

As it was found in the previous paper[1], it is not possible to distinguish between some of the mentioned mechanisms, *e.g.* between the radical mechanism[6,7] and the mechanism which assumes the formation of a ternary complex[3], when the reaction is catalyzed by hydrated metal ions. Therefore, we followed the effect of ligands which yield complexes of different stability with the catalyzing ions, on the initial reaction rate. We found that the effect of these agents corresponds rather to the formation of a competitive equilibrium of the binary complexes of catalyzing ions both with hydroquinone and with hydrogen peroxide and of the ternary complex of all the three components on the one side, and the complex of the catalyst with the complex forming reagent on the other side, than to the assumption that the "masking" of the catalyst in the complex makes impossible the formation of radicals which could

further undergo a chain reaction. In order to make possible a quantitative comparison of experimental results with those predicted theoretically, we have chosen Cu^{2+} as catalyzing ion, in spite of the fact that Fe^{2+} is far more effective as a catalyst in the oxidation with hydrogen peroxide[8]. The reason was that the stability constants of Cu^{2+} complexes are either available in tabellated form or they could be determined by using a selective copper electrode and finally also the fact that cupric ions form only labile complexes[9]. Sodium salts of nitrilotriacetic acid (NTA) and of ethylenediaminetetraacetic acid (EDTA) were used as reference complex forming agents, since their complexes with Cu^{2+} were studied in detail, their composition is 1 : 1, *i.e.* no gradual formation of the complex occurs and finally their stability constants are known. Besides, the stability constants of these complexes can be calculated for various values of pH. Further experiments were performed with some other complexing agents and the results were compared at least qualitatively with the anticipated effect.

EXPERIMENTAL

The chemicals used were of the reagent grade purity or they were purified as described earlier[1]. Apparatus and equipments were the same as used in the previous work[1]. The stability constants of some Cu^{2+} complexes were determined by the modified Leden's method[11] using a selective copper electrode "Crytur" (Monokrystaly, Turnov). Saturated calomel electrode served for reference. EMF was measured with a pH meter (Claman und Grahnert, Dresden, GDR). The electrode was calibrated for $[Cu^{2+}] = 10^{-6}$ to 10^{-1} mol/l and the value of $pCu^{2+} =$ was calculated from the measured EMF (in mV) by means of the linear regression equation $pCu^{2+} = = 10.844 - 4.0837$ (EMF). The value of the regression coefficient $r = -0.99997$ indicates a very close but indirect dependence of the pCu^{2+} on the measured EMF.

When following the reaction course spectrophotometrically, one can determine either the decrease of the substrate concentration $-(d[A]/dt)$, where A = H_2W, H_2P, H_2R or H_2Q in the UV region, by determining metol at $\lambda = 198$ nm, pyrocatechol at 276 mn, resorcinol at 273 nm and hydroquinone at 288 nm, or the formation of coloured products, *i.e.* quinone or its derivatives $+(d[X]/dt)$ in the visible region at 450−475 nm. The products of the reaction of phenols and aminophenols with hydrogen peroxide are dealt with in the paper of Musso[12]. The reaction was followed in the medium of acetate buffer of pH 5·0, at $[CH_3CO_2^-] = 0.016$M. Measurement with glass electrode revealed that pH does not change in this medium in the course of the reaction.

RESULTS AND DISCUSSION

Oxidation of methyl *p*-aminophenol sulphate (metol) (H_2W) with hydrogen peroxide proceeds similarly as in the case of hydroquinone[1] (H_2Q) at a measurable rate only in the presence of Cu^{2+}, Fe^{2+} or Fe^{3+} ions, in the medium in which a not too stable complex of the catalyzing ion is formed. So, *e.g.* the reaction does not proceed in a citrate or Britton–Robinson buffer.

When studying the course of both $+(d[X]/dt)$ and $-(d[A]/dt)$ the initial reaction rate v_0 was determined as the slope of the kinetic curve in the origin of coordinates;

it was found that $v_0 = k[H_2O_2]_0 [Cu^{2+}]_0 [A]_0$, *i.e.* that the initial reaction rate is proportional to the concentration of the catalyzing ion. However, this simple relation is valid only for the ratio $[A]_0/[H_2O_2]_0 = 1$ or close to unity, at a greater excess of the reacting component it is not fulfilled. Since the kinetic study itself does not bring enough information which could prove the plausibility of the different mechanisms, considered previously in the oxidation of hydroquinone with hydrogen peroxide[1], we have followed the dependence of the initial reaction rate v_0 on the concentration of the catalyst as well as the effect of complex forming reagents (L) yielding soluble complexes of various stability with the catalyzing ions (*i.e.* in our case with Cu^{2+}).

Oxidation of metol, pyrocatechol and resorcinol with hydrogen peroxide was slowed down by the presence of NTA or EDTA. The additions of these agents (L) were chosen so as to cause a regular increase of the ratio $[L]_0/[Cu^{2+}]_0$ with respect to the initial concentration of $[Cu^{2+}]_0$. The change of the ratio of the initial reaction rate, catalyzed by a defined amount of the catalyst after addition of the complex forming reagent, v_0, to that of the reaction catalyzed by the same amount of the catalyst but without any reagent added, v_0^*, *i.e.* the change of the ratio (v_0/v_0^*) was studied for different values of $[A]_0/[H_2O_2]_0$, of $[A]_0 + [H_2O_2]/[Cu^{2+}]_0$, for various complex forming reagents (NTA or EDTA) and various substrates: A = $= H_2W$, H_2R, H_2P and in some experiments also H_2Q. These experiments revealed the effect of the stability constant of the complex of the catalyzing ion with the reagent added. So, *e.g.* for $[H_2W] = 1 . 10^{-1}$; $[Cu^{2+}]_0 = 4 . 10^{-3}$ L = EDTA $(K_5 = 2 . 10^{12})$ had the following effect on (v_0/v_0^*) at different ratios $[L]_0/[Cu^{2+}]_0$:

$[L]_0/[Cu^{2+}]_0$	0·167	0·333	0·500	0·667	0·883	0·920
(v_0/v_0^*)	0·712	0·482	0·326	0·204	0·090	0·038
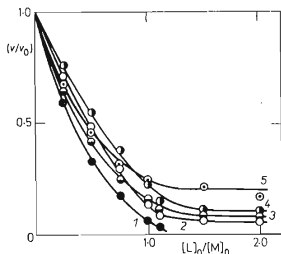
FIG. 1

Dependence of (v_0/v_0^*) on $[L]_0/[Cu^{2+}]_0$ for Various Ratios $[A]_0 + [H_2O_2]_0/[Cu^{2+}]_0 = = P$ and $[A]_0/[H_2O_2]$
1 $P = 2$, $[A]_0 = [H_2O_2]$; *2* $P = 10$, $[A]_0 = [H_2O_2]$; *3* $P = 13·3$, $[A]_0 = [H_2O_2]$ *4* $P = 10$, $[A]_0 = 5[H_2O_2]$; *5* $P = 10$, $5[A]_0 = [H_2O_2]_0$.

whereas L = NTA (K_5 = 1 . 10^7) was by far lower:

$[L]_0/[Cu^{2+}]_0$	0·25	0·50	0·75	1·00	1·10
(v_0/v_0^*)		0·702	0·498	0·300	0·135	0·089

The effect of the initial concentration ratio $[A]_0/[H_2O_2]_0$ can be seen in Fig. 1. The effect of the complex forming reagents differs for various substrates and increases

TABLE I

Dependence of (v_0/v_0^*) on the Ratio $[L]_0/[Cu^{2+}]_0$

Oxidation of metol [H_2W], pyrocatechol [H_2P] and hydroquinone [H_2Q] with hydrogen peroxide; $[A]_0 = [H_2O_2]_0$; $P = ([A]_0 + [H_2O_2]_0)/[M]_0 = 10$; L = NTA.

$\dfrac{[L]_0}{[Cu^{2+}]_0}$	Metol $K_1 = 6 . 10^2$	Pyrocatechol $K_1 = 4 . 10^2$	Hydroquinone $K_1 = 3 . 10^2$
0·00	1·000	1·000	1·000
0·25	0·702	0·600	0·540
0·50	0·498	0·330	0·249
0·75	0·300	0·171	0·094
1·00	0·135	0·030	—[a]
1·10	0·089	—[a]	—[a]

[a] Immeasurably small value of (v_0/v_0^*).

TABLE II

Dependence of (v_0/v_0^*) on $[L]_0/[Cu^{2+}]_0$ at Various Ratios $P = ([A]_0 + [H_2O_2]_0)/[Cu^{2+}]_0$

A = H_2W; H_2Q; L = NTA. A: $P = 2·0$, B: $P = 10$, C: $P = 13·3$, D: $P = 33·3$.

$\dfrac{[L]_0}{[Cu^{2+}]_0}$	Metol			Hydroquinone	
	A	B	C	B	D
0·00	1·000	1·000	1·000	1·000	1·000
0·25	0·590	0·702	0·765	0·551	0·685
0·50	0·325	0·498	0·590	0·249	0·377
0·75	0·180	0·300	0·373	0·094	0·164
1·00	0·070	0·135	0·220	—[a]	0·043

[a] Immeasurably small value of (v_0/v_0^*).

in the sequence $H_2Q < H_2R$, $H_2P < H_2W$. Some values of (v_0/v_0^*) under different conditions are summarised in Tables I—III.

The experimental data were compared with the values calculated for different mechanisms. Fenton's interpretation, *i.e.* that the oxidized substrate forms with the catalyzing ion a complex which is then oxidized by hydrogen peroxide, was later fairly well disproved by kinetic studies[6,7], nevertheless, we have included it in our discussions, at least because all the compounds used as oxidized substrates really form complexes with Cu^{2+}. Their conditional stability constants at pH 5 in acetate buffer at $CH_3CO_2^- = 0.016M$ were determined by means of Leden's method[11], using a selective copper electrode. The found values are presented in the head of Table I. If the oxidation proceeded according to this mechanism, it should hold that for initial concentrations $[A]_0$, $[H_2O_2]_0$, $[Cu^{2+}]_0$ and $[L]_0$ where L denotes the complex forming reagent and for $[A]_0 \gg [Cu^{2+}]_0$ the initial reaction rate is given by

$$v = k[CuA]_0 [H_2O_2]_0 , \qquad (1a)$$

$$v = k\{K_1[A]_0 [Cu^{2+}]_0/[K_1[A]_0 + K_5[L]_0]\} [H_2O_2]_0 , \qquad (1b)$$

where K_1 is the conditional stability constant of the Cu^{2+} complex with the substrate A and K_5 is the stability constant of the complex with the reagent L added. Since all these values, with the exception of rate constant k are known, we are able to estimate the course of the dependence of (v_0/v_0^*), expressed by the relation

$$(v_0/v_0^*) = K_1[A]_0/(K_1[A]_0 + K_5[L]_0) , \qquad (2)$$
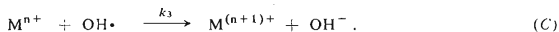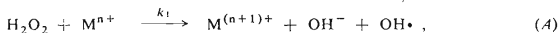
TABLE III

Dependence of (v_0/v_0^*) on the Ratio of the Initial Concentrations of the Components
$[H_2W]_0 = 1 . 10^{-1}$ mol/l; $[Cu^{2+}]_0 = 4 . 10^{-3}$ mol/l; $P = 10$; $L = NTA$.

$\dfrac{[L]_0}{[Cu^{2+}]_0}$	$[H_2W] = [H_2O_2]$	$[H_2W] = 5[H_2O_2]$	$5[H_2W] = [H_2O_2]$
0.0	1.000	1.000	1.000
2.25	0.702	0.688	0.660
0.50	0.498	0.474	0.410
0.75	0.300	0.325	0.250
1.00	0.135	0.252	0.140
1.10	0.089	0.228	0.120
1.50	*a*	0.219	0.105
2.00	*a*	0.175	0.069

a Immeasurably small value of (v_0/v_0^*).

on the value of the ratio $[L]_0/[Cu^{2+}]_0$. However, Eq. (2) does not contain the term $[Cu]_0$ which is in contradiction with experimental results. What is still more important is that the real change of (v_0/v_0^*) with $[L]_0/[Cu^{2+}]_0$ for known values of K_1, K_5, $[A]_0$ and $[L]_0$ entirely disagrees with the calculated values, as can be seen in Fig. 2. An agreement of the calculated values with the measured ones could only be obtained in the case that $K_1 = K_5$, which however is in sharp contrast with the experimentally found value of K_1. Moreover, even in this case the agreement cannot be attained both for NTA ($K_5 = 10^7$) and simultaneously for EDTA ($K_5 = 2 . 10^{12}$). Consequently the Fenton's interpretation cannot be accepted.

The radical mechanism, which is still very often reported, is based on the assumption that the rate determining process in the oxidation with peroxide is the formation of OH· and O_2H· radicals as a result of the effect of the catalyst on hydrogen peroxide, according to reactions

$$H_2O_2 + M^{n+} \xrightarrow{k_1} M^{(n+1)+} + OH^- + OH\cdot , \qquad (A)$$

$$H_2O_2 + M^{n+1} \xrightarrow{k_2} M^{n+} + H^+ + O_2H\cdot , \qquad (B)$$

$$M^{n+} + OH\cdot \xrightarrow{k_3} M^{(n+1)+} + OH^- . \qquad (C)$$

Radicals OH· or O_2H· react then fast with the substrate. If reaction (A) is the rate determining process then for M = Cu^{2+} and provided a steady state is attained ($d[OH\cdot]/dt = 0$ and $d[O_2H\cdot]/dt = 0$) the reaction rate is

$$v_0 = k_1\{[Cu^{2+}]_0 [H_2O_2]_0 [A]_0/(k_2[A]_0 + k_3[Cu^{2+}]_0) . \qquad (3)$$

If $[A]_0 = [H_2O_2]_0$ and $(k_2[A]_0 + k_3[Cu^{2+}]_0) = $ const., which holds for the initial reaction rate, then

$$v_0 = k_A[Cu^{2+}]_0 , \qquad (4)$$

where $k_A = k_1\{[A]_0 [H_2O_2]/(k_2[A]_0 + k_3[Cu^{2+}]_0)\}$, which indeed agrees with the experimental results for $[Cu^{2+}]_0 \ll [A]_0$. In this case, however, it should also hold that $(v_0/v_0^*) = [Cu^{2+}]/[Cu^{2+}]_0$, even if a part of the Cu^{2+} ions are incorporated in the complex CuL, i.e. if $[Cu^{2+}] = [Cu^{2+}]_0/(K[L]_0 + 1)$. The disagreement for $[L]_0/[Cu^{2+}]_0 \geq 1$ can be clearly seen in Fig. 2. If the radical mechanism were valid then $-\log v_0$ should necessarily change with $-\log [Cu^{2+}]$, according to the titration curve of Cu^{2+} with the complex forming reagents, i.e. NTA or EDTA. Actually, (v_0/v_0^*) for $[L]_0/[Cu^{2+}]_0 = 1$ does not change abruptly, as $[Cu^{2+}]$: : $[Cu^{2+}]_0$ does during titration, but on the contrary even less than for the lowest values of $[L]_0/[Cu^{2+}]_0$ and for $[L]_0/[Cu^{2+}]_0 < 1$ its change is only negligible.

The same disagreement has already been mentioned in paper[1]. Moreover, the radical mechanism can scarcely explain why the differences between the different substrates make themselves significant in the sequence $H_2Q < H_2R$, $H_2P < H_2W$ which simultaneously corresponds to the series of values of the stability constant K_1 of these compounds with Cu^{2+} (Table I).

A mechanism, which considered the interaction of two binary complexes of the catalyst with both compounds, i.e. CuA and $Cu.H_2O_2$, cannot be accepted for the very reason that in this mechanism $v_0 = k'[Cu^{2+}]_0^2$. However, for all compounds studied a linear dependence was found of v_0 on $[Cu^{2+}]_0$, at least for $[Cu^{2+}]_0 \ll \ll [A]_0$, and for $[Cu^{2+}]_0 \approx [A]_0$ a deviation from linearity towards slower course. Besides, the linearity of the dependence of the initial reaction rate of hydroquinone oxidation on $[Fe^{2+}]_0$ was verified already in the previous paper[1] by testing at the significance level $\alpha = 0.95$ and consequently the above mentioned mechanism was rejected as improbable.

The mechanism, proposed by Michaelis and Menten[3] for enzymatically catalyzed reactions, was chosen as the most probable[1] for interpretation of the oxidation of hydroquinone with peroxide, catalyzed by Fe^{2+} or Cu^{2+}. This mechanism assumes formation of binary complexes of the catalyzing metal with the components, followed by interaction of these binary complexes with the second component yielding a ternary complex which upon decomposition leads to the first product and the free catalyzing ion. The second and further products are then formed in the reaction of the first product with the components. If we take into consideration also the formation of a complex of the catalyst with the complex forming reagent L which is added in order to follow the existing equilibrium we can describe the over-all mechanism by the following scheme[10] (D):

$$ML \underset{K_5}{\overset{L}{\rightleftharpoons}} M \xrightarrow[]{} AMO_2H \xrightarrow{k_1} X \xrightarrow{k_2} Y \qquad (D)$$
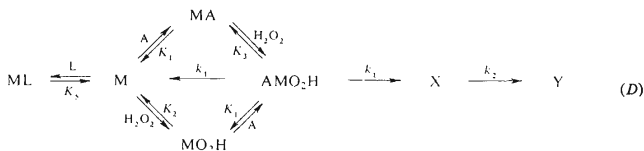
According to this scheme and since in our case $M = Cu^{2+}$, we can write

$$v_0 = k\{(K_1K_3 + K_2K_4)[Cu^{2+}]_0[A]_0[H_2O_2]_0/(1 + K_1[H_2O_2]_0 + K_2[A]_0 + (K_1K_3 + K_2K_4)[H_2O_2]_0[A]_0)\}. \qquad (5)$$

Provided that $K_1[H_2O_2]_0 + K_2[A]_0 + (K_1K_3 + K_2K_4)[A]_0[H_2O_2]_0 = $ const.

which holds for the initial reaction rate Eq. (5) assumes the form which was both experimentally found and theoretically verified

$$v_0 = k^*[Cu^{2+}]_0 [A]_0 [H_2O_2]_0 , \qquad (6)$$

where $k^* = k\{(K_1K_3 + K_2K_4)/(1 + K_1[H_2O_2]_0 + K_2[A]_0 + (K_1K_3 + K_2K_4)$. $. [A]_0 [H_2O_2]_0)\}.$

The course of the reaction according to Scheme (D) was followed on a computer using a programme set up so that the given mechanism is automatically transformed into a system of differential equations which is then numerically solved by means of the modified Euler method. The result is the time dependence of the concentrations of all participating components, *i.e.* of the initial compounds, intermediates and final products. The corresponding algebraic equations are computed by iteration method.

The advantage of the mentioned procedure is that no rate determining reaction need to be assumed. However, it is indispensable to know the rate or equilibrium constants of all reactions, participating in the mechanism. In practice some experimentally determined constants and others taken from the literature or only estimated
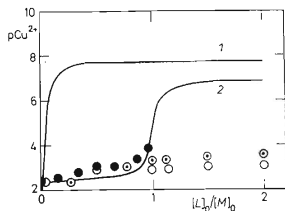
Fig. 2

Comparison of Experimental Results with the Theory for Fenton's and Radical Mechanism; Equilibrium $MA + L \rightleftharpoons ML + A$; $L = NTA$

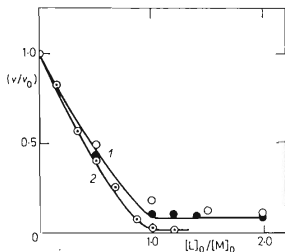*1* Theory for Fenton's mechanism, *2* theory for radical mechanism; experimental points: ○ metol, ● hydroquinone, ⊙ pyrocatechol.

Fig. 3

Comparison of the Experimentally Found Dependence of (v_0/v_0^*) on $[L]_0/[Cu^{2+}]_0$ with the Calculated One for the Case of Oxidation of Metol with Peroxide

Experimental points: ● $P = 10$, $[A]_0 = [H_2O_2]_0$; complex forming reagent NTA. ○ $P = 13\cdot3$, $[A]_0 = [H_2O_2]_0$; complex forming reagent NTA; ⊙ $P = 10$, $[A_0] = [H_2O_2]_0$, complex forming reagent EDTA. Curve *1* was computed for NTA, curve *2* for EDTA.

values can be used. In our case, the constants K_1, K_2 and K_5 were either known or they were determined, K_3, K_4, k_1 and k_2 were estimated and substituted so as to make the course of $d[A]/dt$ or $d[X]/dt$ most closely similar to the experimentally found kinetic conditions. v_0^* was calculated and its value was compared with the experimentally found values for various conditions, as well as the found dependence of v_0 on $[Cu^{2+}]_0$ and the dependence of (v_0/v_0^*) on $[L]_0/[Cu^{2+}]_0$. The values for K_1 were taken from Table I, K_2 was set equal 10^{-2} and $K_5 = 10^7$ for NTA and $2 . 10^{12}$ for EDTA, which is in accordance with the conditional constants for pH 5. Graphical comparison of the calculated dependence (v_0/v_0^*) on $[L]_0/[Cu^{2+}]_0$ with the found one is shown in Fig. 3. It is evident that in spite of the fact that the model according to Scheme (D) undoubtedly involves a certain simplification (equilibria, characterized by constants K_1 to K_5 are considered instantaneous, no formation of higher binary complexes is taken into account, e.g. $M + A \rightarrow MA$, $MA + A \rightarrow MA_2$ etc., no possibility of the change of valence of the catalyst and consequently also no change of the values of $K_1 - K_5$ in the course of the reaction is assumed), the agreement of the computed results with the experimentally found ones is very good. In addition to NTA and EDTA, the following complex forming reagents were used already in the first paper[1]: citric acid, oxalic acid, sulphosalicylic acid and recently also histamine in the present paper. Their effect was found to be practically the same as in the case of hydroquinone oxidation. However, a quantitative comparison for these complex-forming reagents could not be performed since in this case a stepwise formation of complexes probably takes place.

The accepted mechanism (D) also makes it possible to interpret some of the experimentally found, but hitherto not plausibly elucidated phenomena. So, e.g. the fact that different metal ions affect to a different extent the oxidation of various organic substances with hydrogen peroxide, is well known and it has also been analytically exploited[13]. This phenomenon could of course not be explained by radical mechanism, whereas the mechanism proposed in the present paper offers a quite easy explanation. If the reaction should take place, a ternary complex must necessarily be formed and its formation or its stability is reflected as a certain selectivity of the catalyst.

REFERENCES

1. Eckschlager K., Vepřek-Šiška J.: This Journal *38*, 1623 (1973).
2. Strelcova E. M., Petrašeň V. J.: Ž. Anal. Chim. *20*, 1169 (1965).
3. Michaelis L., Menten M. L.: Biochem. Z. *49*, 333 (1913).
4. Vepřek-Šiška J., Hasnedl A., Mádlo K.: This Journal *36*, 3096 (1971).
5. Wágnerová D. M., Schwertnerová E., Vepřek-Šiška J.: This Journal *38*, 756 (1973).
6. Haber F., Willstädter R.: Ber. *64*, 2844 (1931).
7. Haber F., Weiss J.: Proc. Roy. Soc. (London) A *147*, 332 (1932).
8. Fenton J.: J. Chem. Soc. *65*, 899 (1894).
9. Taube H.: Chem. Rev. *50*, 69 (1952).

10. Laidler K. J., Bunting P. S.: *The Chemical Kinetics of Enzyme Action*, p. 114, 2nd. Ed. Oxford University Press, Oxford 1973.
11. Leden J.: Acta Chim. Scand. *3*, 1318 (1949); *10*, 541 (1956).
12. Musso H.: Angew. Chem. *75*, 965 (1963).
13. Jacimirskij K. B.: *Kinetics Methods of Analysis*, p. 216. Pergamon Press, Oxford 1966.
14. Bjerrum J., Schwarzenbach G., Sillén L. G.: *Stability Constants*. The Chemical Society, London 1967.

Translated by V. Čermáková.