

THE CATALYTIC DECOMPOSITION OF HYDROGEN PEROXIDE BY MIXED CATALYSTS

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INTRODUCTION

The catalytic decomposition of hydrogen peroxide by a mixture of homogeneous catalysts constitutes a problem which has not yet been finally solved. A. C. Robertson (10) has explained the promoter effect of cations on the catalytic decomposition by assuming that the valence of the cation is increased in an intermediary product. However, Haber and Weiss (6) considered this assumption to be insufficiently established. Recent work in this field has failed to provide an unequivocal explanation of the reaction mechanism involved. In the present investigation the catalytic decomposition of hydrogen peroxide by sodium tungstate and sodium molybdate in the presence of cations and of their complexes has been studied. Cupric ion was found to be the most active cation, whether present as such or in a complex. The aim of this study was to provide a general picture of the reaction mechanism of the catalytic decomposition of hydrogen peroxide and to explain phenomena which are characteristic of this process.

THE CATALYTIC DECOMPOSITION OF HYDROGEN PEROXIDE BY SODIUM TUNGSTATE AND SODIUM MOLYBDATE IN THE PRESENCE OF SIMPLE CATIONS

Sodium tungstate (or sodium molybdate) by itself exerts only a very feeble effect on hydrogen peroxide. Addition of acetic acid in equivalent amounts depresses the decomposition of hydrogen peroxide almost completely. Decomposition nevertheless occurs in equal conditions of pH in the additional presence of certain cations and their complexes. The influence of the following cations was investigated: Cu^{++} , Co^{++} , Ni^{++} , Mn^{++} , Cd^{++} , Zn^{++} .

The gasometric measurements were carried out with the aid of an apparatus constructed in this laboratory (5). Most of the experiments were done in paraffined reaction vessels. The reaction vessels were kept in a thermostat at a temperature of 15°C . ($\pm 0.1^\circ$). The volume of the solutions was 20 cc. Hydrogen peroxide was added to the reaction mixtures as the last component. The gas volumes measured in microburets were calculated to standard conditions of temperature and pressure (N.T.P.).

Table 1 summarizes the results of experiments with the cations which have been mentioned. The influence of ferric ions was not further investigated, since precipitates or suspensions are formed in the presence of ferric ion which fail to dissolve in weakly acid solutions, and it would be incorrect to class these cases under true homogeneous catalysis.

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The composition of the last mixtures is shown in table 1. $T_{1/2}$ represents the time in which half of the amount of hydrogen peroxide initially added is decomposed, and $T_{1/4}$ the time in which the first quarter of the initially added hydrogen peroxide is decomposed. The difference $T_{1/2} - T_{1/4} = \tau^*$ shows the time of decomposition of the second quarter of the amount of hydrogen peroxide initially added. The last value is independent of the duration of the induction period and is therefore suitable for the determination of the reaction order. The monomolecular velocity constants calculated according to the formula $k = \ln 1.5/\tau^*$ conform to the reaction curves. The data shown in table 1 make

TABLE 1

Effect of various cations on the rate of decomposition of hydrogen peroxide

Paraffined vessels; $t = 15^\circ\text{C}$.; volume† = 20 cc.

Na_2WO_4 ($M/10$)	CH_3COOH ($M/10$)	MeSO_4 or $\text{Me}(\text{NO}_3)_2$	H_2O_2 ($2 M$)	$T_{1/4}$	$T_{1/2}$	$T_{1/2} - T_{1/4}$ $= \tau^*$
cc.	cc.		cc.	min.	min.	min.
1	2	1 cc. $M/10$ $\text{Cu}(\text{NO}_3)_2$	1	20	38	18
1	2	5 cc. $M/100$ $\text{Cu}(\text{NO}_3)_2$	1	32	60	28
1	2	1 cc. $M/100$ $\text{Cu}(\text{NO}_3)_2$	1	54	105	51
1	2	1 cc. $M/10$ $\text{Co}(\text{NO}_3)_2$	1	48		
1	2	1 cc. $M/10$ $\text{Ni}(\text{NO}_3)_2$	1	56		
1	2	1 cc. $M/10$ MnSO_4	1	72		
1	2	1 cc. $M/10$ $\text{Cd}(\text{NO}_3)_2$	1			†
1	2	1 cc. $M/10$ $\text{Zn}(\text{NO}_3)_2$	1			†
	2	1 cc. $M/10$ $\text{Cu}(\text{NO}_3)_2$	1			§
<hr/>						
Na_2MoO_4 ($M/10$)						
cc.						
1		1 cc. $M/10$ $\text{Cu}(\text{NO}_3)_2$	1	13	27	14
1	2	1 cc. $M/10$ $\text{Co}(\text{NO}_3)_2$	1	46		
1	2	1 cc. $M/10$ $\text{Ni}(\text{NO}_3)_2$	1	51		
1	2	1 cc. $M/10$ MnSO_4	1	73		
1	2	1 cc. $M/10$ $\text{Cd}(\text{NO}_3)_2$	1			†
1	2	1 cc. $M/10$ $\text{Zn}(\text{NO}_3)_2$	1			†

† The amount of water added is not quoted in the table.

‡ No decomposition.

§ Decomposition very slow.

it evident that the differences between the influence of sodium tungstate and that of sodium molybdate are small and only quantitative in nature. Cupric ion was by far the most active cation. All the other cations tested showed only small activity, and since experiments with them must be prolonged for many hours, accurate investigation of reaction mechanism in the presence of such cations is difficult. The influence of cupric ion, the most active of the cations, was investigated in greater detail.

Figure 1 presents the course of the reaction curves obtained in the presence of different concentrations of copper. It may be mentioned in this connection that sulfate, nitrate, or acetate ions exert no measurable influence on the reaction

velocity. The reaction curves follow a monomolecular course. The implication of the data will be discussed later.

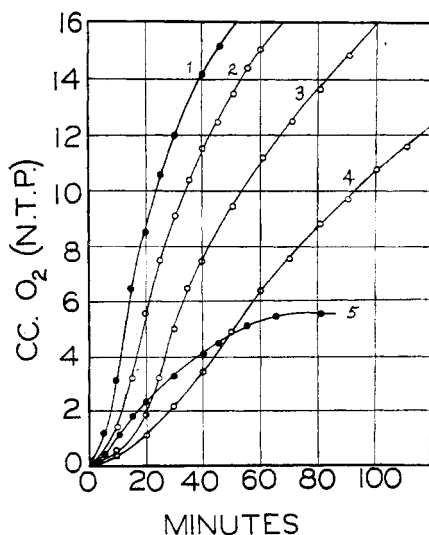


FIG. 1. Decomposition of hydrogen peroxide in the presence of different concentrations of cupric ion. Volume = 20 cc.; $t = 15^{\circ}\text{C}$.; paraffined vessels.

NO.	COMPOSITION OF REACTION MIXTURES
1.....	1 cc. $M/10 \text{ Na}_2\text{MoO}_4$ + 2 cc. $M/10 \text{ CH}_3\text{COOH}$ + 1 cc. $M/10 \text{ Cu}(\text{NO}_3)_2$ + 1 cc. $2 \text{ M H}_2\text{O}_2$ + 15 cc. H_2O
2.....	1 cc. $M/10 \text{ Na}_2\text{WO}_4$ + 2 cc. $M/10 \text{ CH}_3\text{COOH}$ + 1 cc. $M/10 \text{ Cu}(\text{NO}_3)_2$ + 1 cc. $2 \text{ M H}_2\text{O}_2$ + 15 cc. H_2O
3.....	1 cc. $M/10 \text{ Na}_2\text{WO}_4$ + 2 cc. $M/10 \text{ CH}_3\text{COOH}$ + 5 cc. $M/100 \text{ Cu}(\text{NO}_3)_2$ + 1 cc. $2 \text{ M H}_2\text{O}_2$ + 11 cc. H_2O
4.....	1 cc. $M/10 \text{ Na}_2\text{WO}_4$ + 2 cc. $M/10 \text{ CH}_3\text{COOH}$ + 1 cc. $M/100 \text{ Cu}(\text{NO}_3)_2$ + 1 cc. $2 \text{ M H}_2\text{O}_2$ + 15 cc. H_2O
5.....	1 cc. $M/10 \text{ Na}_2\text{MoO}_4$ + 2 cc. $M/10 \text{ CH}_3\text{COOH}$ + 1 cc. $M/10 \text{ Cu}(\text{NO}_3)_2$ + 1 cc. $0.5 \text{ M H}_2\text{O}_2$ + 15 cc. H_2O

THE ACTION OF CHLORO-COMPLEXES IN THE PRESENCE OF SODIUM TUNGSTATE AND SODIUM MOLYBDATE

Chloro-complexes of the following cations formed in concentrated chloride solutions were examined: Cu^{++} , Co^{++} , Ni^{++} , Mn^{++} , Cd^{++} , Zn^{++} . As in the case of the simple cations the cupric chloro-complex showed the highest activity and was therefore investigated in greater detail. Cupric chloro-complex by itself is a powerful catalyst of hydrogen peroxide decomposition (2). The catalytic influence of cupric chloro-complex is almost completely destroyed, however, in weakly acid solutions at a pH of 4.5–5. In the presence of sodium tungstate or sodium molybdate, the cupric chloro-complex exerts a strong catalytic effect even at a pH of 4.5–5. Chloride ions by themselves have only a very small in-

fluence even at high concentration of alkali chloride. The results of the experiments are summarized in table 2. Figure 2 presents the course of several of the reaction curves.

The experiments were carried out in the presence of a large excess of buffer solution ($\text{pH} = 4.63$) in order to ensure maintenance of a constant pH. The concentration of sodium chloride was 3 *N*. It is seen that $\tau^* = T_{1/2} - T_{1/4}$ is independent of the initial concentration of hydrogen peroxide. This proves that the hydrogen peroxide decomposition follows a monomolecular course. The constant $k = \ln 1.5/\tau^*$ of the reaction curves is approximately proportional to the square root of the concentration of the tungstate or molybdate. Also, the relationship between k and the cupric-ion concentration is not a linear one. Sodium tungstate

TABLE 2

Effect of chloro-complexes on the rate of decomposition of hydrogen peroxide

Glass vessels; $t = 15^\circ\text{C}.$; volume = 20 cc.

Na_2WO_4 (<i>M</i> /10)	CH_3COOH (2 <i>M</i>)	CH_3COONa (2 <i>M</i>)	$\text{Cu}(\text{NO}_3)_2$ (<i>M</i> /100)	NaCl (4 <i>M</i>)	H_2O_2 (2 <i>M</i>)	$\tau^* =$ $T_{1/2} - T_{1/4}$
cc.	cc.	cc.	cc.	cc.	cc.	min.
1	1	1	1	15	1	†
1	1	1	1	15	1	‡
1	1	1	1	1	1	168
1	1	1	1	15	1	4.5
1	1	1	0.1	15	1	17
0.1	1	1	1	15	1	12.5
1	1	1	1	15	0.25	4.5
1	1	1	1	5	1	15
Na_2MoO_4 (<i>M</i> /10)						
1	1	1	1	15	1	3.6
1	1	1	1	1	1	128
1	1	1	1	15	0.25	3.7

† $T_{1/10} = 75$ min.

‡ $T_{1/20} = 90$ min.

and sodium molybdate again showed only small quantitative differences. Experiments in glass vessels and in paraffined vessels gave identical results. The comparison of the catalytic effect of simple cupric ion and of cupric chloro-complex in the presence of sodium tungstate or sodium molybdate in the same conditions of pH shows that the velocity constants are about forty times as great in mixtures containing an end concentration of sodium chloride of 3 *N* as in mixtures containing no sodium chloride whatsoever.

THE CATALYTIC ACTION OF COMPLEX CITRATES IN THE PRESENCE OF SODIUM TUNGSTATE OR SODIUM MOLYBDATE

Table 3 presents the results of experiments with citrate complexes of the cations Cu^{++} , Co^{++} , Ni^{++} , Mn^{++} , Cd^{++} , Zn^{++} . All experiments were carried out

in the presence of acetic acid at a concentration equivalent to that of the tungstate and molybdate.³ As there were only small quantitative differences between the results obtained with sodium tungstate and sodium molybdate, respectively, only the data of the tungstate experiments are presented in table 3. In this

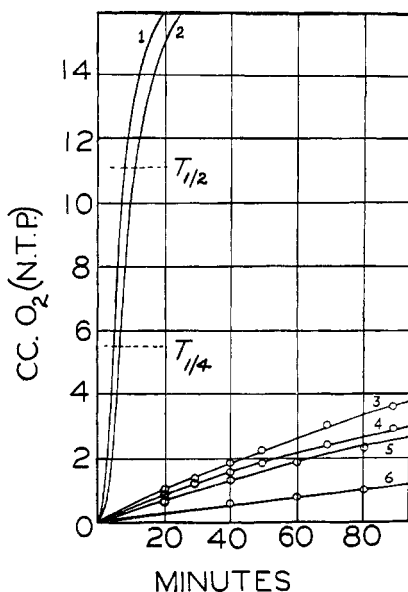


FIG. 2. Effect of chloro-complexes on the decomposition of hydrogen peroxide. Volume = 20 cc.; $t = 15^{\circ}\text{C}$.; glass vessels.

NO.	COMPOSITION OF REACTION MIXTURES
1.....	1 cc. $M/10 \text{ Na}_2\text{MoO}_4$ + 1 cc. $2 M \text{ CH}_3\text{COOH}$ + 1 cc. $2 M \text{ CH}_3\text{COONa}$ + 1 cc. $M/100 \text{ Cu}(\text{NO}_3)_2$ + 15 cc. $4 M \text{ NaCl}$ + 1 cc. $2 M \text{ H}_2\text{O}_2$
2.....	1 cc. $M/10 \text{ Na}_2\text{WO}_4$ + 1 cc. $2 M \text{ CH}_3\text{COOH}$ + 1 cc. $2 M \text{ CH}_3\text{COONa}$ + 1 cc. $M/100 \text{ Cu}(\text{NO}_3)_2$ + 15 cc. $4 M \text{ NaCl}$ + 1 cc. $2 M \text{ H}_2\text{O}_2$
3.....	1 cc. $M/10 \text{ Na}_2\text{MoO}_4$ + 1 cc. $2 M \text{ CH}_3\text{COOH}$ + 1 cc. $2 M \text{ CH}_3\text{COONa}$ + 1 cc. $M/100 \text{ Cu}(\text{NO}_3)_2$ + 1 cc. $2 M \text{ H}_2\text{O}_2$ + 15 cc. H_2O
4.....	1 cc. $M/10 \text{ Na}_2\text{WO}_4$ + 1 cc. $2 M \text{ CH}_3\text{COOH}$ + 1 cc. $2 M \text{ CH}_3\text{COONa}$ + 1 cc. $M/100 \text{ Cu}(\text{NO}_3)_2$ + 1 cc. $2 M \text{ H}_2\text{O}_2$ + 15 cc. H_2O
5.....	1 cc. $2 M \text{ CH}_3\text{COOH}$ + 1 cc. $2 M \text{ CH}_3\text{COONa}$ + 1 cc. $M/100 \text{ Cu}(\text{NO}_3)_2$ + 15 cc. $4 M \text{ NaCl}$ + 1 cc. $2 M \text{ H}_2\text{O}_2$ + 1 cc. H_2O
6.....	1 cc. $M/10 \text{ Na}_2\text{WO}_4$ + 1 cc. $2 M \text{ CH}_3\text{COOH}$ + 1 cc. $2 M \text{ CH}_3\text{COONa}$ + 15 cc. $4 M \text{ NaCl}$ + 1 cc. $2 M \text{ H}_2\text{O}_2$ + 1 cc. H_2O

series of experiments, as in the previous cases, the cupric complex proved to be by far the most active, and was therefore investigated in greater detail. Comparison of the results of tables 3 and 1 shows that the activity of the cupric citrate

³Acetate ion in this concentration does not exert any influence on the catalytic decomposition.

complex in relation to that of the simple cupric ion is approximately as 10:1. It is of interest that the cupric citrate complex itself does not decompose hydro-

TABLE 3

Effect of citrate complexes on the rate of decomposition of hydrogen peroxide

Paraffined vessels; $t = 15^\circ\text{C}.$; volume = 20 cc.

Na_2WO_4 ($M/10$)	CH_3COOH ($M/10$)	$M/10 \text{ Me}(\text{NO}_3)_2$ or $M/10 \text{ MeSO}_4$	Na_3Cl ($M/10$)	H_2O_2 ($2 M$)	$T_{1/4}$	$T_{1/2}$	$\tau^* = T_{1/2} - T_{1/4}$
cc.	cc.		cc.	cc.	min.	min.	min.
1	2			1			†
1	2		1	1			†
1	2	1 cc. $M/10 \text{ Cu}(\text{NO}_3)_2$	1	1	2.1	4.5	2.4
1	2	1 cc. $M/10 \text{ Co}(\text{NO}_3)_2$	1	1	12.5	23	10.5
1	2	1 cc. $M/10 \text{ Ni}(\text{NO}_3)_2$	1	1	40	87	47
1	2	1 cc. $M/10 \text{ MnSO}_4$	1	1			‡
1	2	1 cc. $M/10 \text{ Cd}(\text{NO}_3)_2$	1	1			†
1	2	1 cc. $M/10 \text{ Zn}(\text{NO}_3)_2$	1	1			†

† No decomposition.

‡ Decomposition very slow.

TABLE 4

Catalytic effect of the cupric citrate complex on the decomposition of hydrogen peroxide

Paraffined vessels; $t = 15^\circ\text{C}.$; volume = 20 cc.

Na_2WO_4	CH_3COOH	$\text{Cu}(\text{NO}_3)_2$	Na_3Cl	H_2O_2 ($2 M$)	$T_{1/4}$	$T_{1/2}$	$\tau^* = T_{1/2} - T_{1/4}$
				cc.	min.	min.	min.
1 cc. $M/10$	2 cc. $M/10$	1 cc. $M/10$	1 cc. $M/10$	1	2.1	4.5	2.4
1 cc. $M/10$	2 cc. $M/10$	1 cc. $M/10$	1 cc. $M/10$	0.5	2.2	4.7	2.5
1 cc. $M/10$	2 cc. $M/10$	1 cc. $M/10$	1 cc. $M/10$	2.0	1.9	4.3	2.4
0.5 cc. $M/10$	1 cc. $M/10$	1 cc. $M/10$	1 cc. $M/10$	1	3.8	7.2	3.4
1 cc. $M/100$	2 cc. $M/100$	1 cc. $M/10$	1 cc. $M/10$	1	10.3	17.8	7.5
1 cc. $M/1000$	2 cc. $M/1000$	1 cc. $M/10$	1 cc. $M/10$	1	48	73	25
1 cc. $M/10$	2 cc. $M/10$	0.5 cc. $M/10$	0.5 cc. $M/10$	1	4.0	7.8	3.8
1 cc. $M/10$	2 cc. $M/10$	1 cc. $M/100$	1 cc. $M/100$	1	18.4	27	8.6
1 cc. $M/10$	2 cc. $M/10$	1 cc. $M/10$	0.5 cc. $M/10$	1	2.4	5.4	3.0
1 cc. $M/10$	2 cc. $M/10$	1 cc. $M/10$	1 cc. $M/100$	1	3.6	7.8	4.2
1 cc. $M/10$	2 cc. $M/10$	1 cc. $M/10$	1 cc. $M/1000$	1	9.5	19.0	9.5
		1 cc. $M/10$	1 cc. $M/10$	1			†
Na_2MoO_4							
1 cc. $M/10$	2 cc. $M/10$	1 cc. $M/10$	1 cc. $M/10$	1	1.9	4.1	2.2

† No decomposition.

gen peroxide, contrasting in this respect with ferric citrate and cobaltous citrate complexes.

Table 4 presents data concerning the catalytic effect of the cupric citrate complex at different concentrations of hydrogen peroxide, sodium tungstate, cupric ion, and trisodium citrate (Na_3Ci). Figure 3 presents several reaction curves with cupric citrate and sodium tungstate at different concentrations. It may be seen from the values presented in table 4 that the catalytic decomposition conforms to a reaction of the first order with respect to the hydrogen perox-

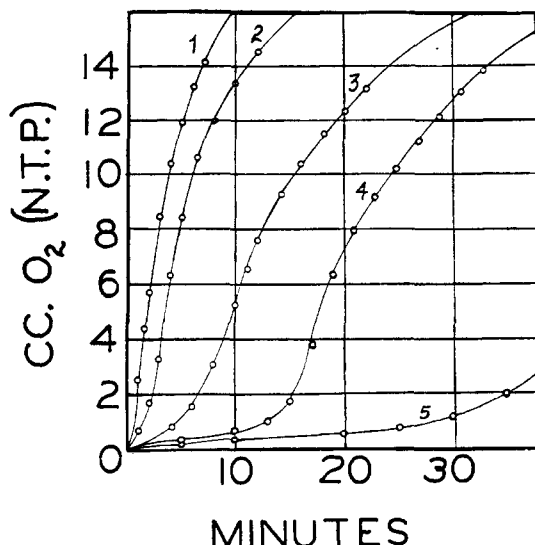


FIG. 3. Effect of cupric citrate and sodium tungstate at different concentrations on the decomposition of hydrogen peroxide. Volume = 20 cc.; $t = 15^\circ\text{C}$.; paraffined vessels.

NO.	COMPOSITION OF REACTION MIXTURES
1.....	1 cc. $M/10 \text{ Na}_2\text{WO}_4$ + 2 cc. $M/10 \text{ CH}_3\text{COOH}$ + 1 cc. $M/10 \text{ Cu}(\text{NO}_3)_2$ + 1 cc. $M/10 \text{ Na}_3\text{Ci}$ + 1 cc. 2 $M \text{ H}_2\text{O}_2$ + 14 cc. H_2O
2.....	0.5 cc. $M/10 \text{ Na}_2\text{WO}_4$ + 1 cc. $M/10 \text{ CH}_3\text{COOH}$ + 1 cc. $M/10 \text{ Cu}(\text{NO}_3)_2$ + 1 cc. $M/10 \text{ Na}_3\text{Ci}$ + 1 cc. 2 $M \text{ H}_2\text{O}_2$ + 15.5 cc. H_2O
3.....	1 cc. $M/100 \text{ Na}_2\text{WO}_4$ + 2 cc. $M/100 \text{ CH}_3\text{COOH}$ + 1 cc. $M/10 \text{ Cu}(\text{NO}_3)_2$ + 1 cc. $M/10 \text{ Na}_3\text{Ci}$ + 1 cc. 2 $M \text{ H}_2\text{O}_2$ + 14 cc. H_2O
4.....	1 cc. $M/10 \text{ Na}_2\text{WO}_4$ + 2 cc. $M/10 \text{ CH}_3\text{COOH}$ + 1 cc. $M/100 \text{ Cu}(\text{NO}_3)_2$ + 1 cc. $M/100 \text{ Na}_3\text{Ci}$ + 1 cc. 2 $M \text{ H}_2\text{O}_2$ + 14 cc. H_2O
5.....	1 cc. $M/1000 \text{ Na}_2\text{WO}_4$ + 2 cc. $M/1000 \text{ CH}_3\text{COOH}$ + 1 cc. $M/10 \text{ Cu}(\text{NO}_3)_2$ + 1 cc. $M/10 \text{ Na}_3\text{Ci}$ + 1 cc. 2 $M \text{ H}_2\text{O}_2$ + 14 cc. H_2O

ide concentration, the value of τ^* being a constant. With $\text{Cu}^{++}:\text{Na}_3\text{Ci}$ as 1:1 the velocity constant $k = \ln 1.5/\tau^*$ corresponding to the reaction curves is approximately proportional to the square root of the concentration of sodium tungstate and of cupric citrate.

Very small amounts of citrate suffice to activate the cupric ion. At a citrate concentration of $M/20,000$ and with $\text{Cu}^{++}:\text{Na}_3\text{Ci}$ as 100:1, the reaction velocity is roughly twice as high as in the absence of citrate (compare table 1).

THE INDUCTION PERIOD

A special phenomenon is observed when the relationship $\text{Na}_3\text{Ci}:\text{Cu}^{++}$ exceeds 1:1. In the presence of an excess of trisodium citrate an induction period⁴ which may last for several minutes to several hours is observed. During the induction

TABLE 5

Study of the induction period observed in the catalytic decomposition of hydrogen peroxide by ferric citrate

Unless defined otherwise $t = 15^\circ\text{C}$. and volume = 20 cc.

REACTION VESSEL	Na_2WO_4	CH_3COOH	$\text{Cu}(\text{NO}_3)_2$	Na_3Ci	H_2O_2 (2 M)		
					cc.	$t^* - T_{1/2}$ min.	INDUC- TION PERIOD min.
Paraffined.....	1 cc. M/10	2 cc. M/10	1 cc. M/10	1 cc. M/10	1	2.4	<1
Glass (trans- parent).....	1 cc. M/10	2 cc. M/10	1 cc. M/10	1 cc. M/10	1	2.4	<1
Glass (black)...	1 cc. M/10	2 cc. M/10	1 cc. M/10	1 cc. M/10	1	2.4	<1
Paraffined.....	1 cc. M/10	2 cc. M/10	1 cc. M/10	1.5 cc. M/10	1	2.5	3.5
Glass (trans- parent).....	1 cc. M/10	2 cc. M/10	1 cc. M/10	1.5 cc. M/10	1	2.5	32
Glass (black)...	1 cc. M/10	2 cc. M/10	1 cc. M/10	1.5 cc. M/10	1	2.5	9.5
Paraffined.....	1 cc. M/10	2 cc. M/10	1 cc. M/10	2.0 cc. M/10	1	2.5	7.5
Glass (trans- parent).....	1 cc. M/10	2 cc. M/10	1 cc. M/10	2.0 cc. M/10	1	2.5	68
Glass (black)...	1 cc. M/10	2 cc. M/10	1 cc. M/10	2.0 cc. M/10	1	2.5	23
Paraffined.....	1 cc. M/10	2 cc. M/10	1 cc. M/10	2.5 cc. M/10	1	2.5	29
Glass (trans- parent).....	1 cc. M/10	2 cc. M/10	1 cc. M/10	2.5 cc. M/10	1	2.5	>120
Glass (black)...	1 cc. M/10	2 cc. M/10	1 cc. M/10	2.5 cc. M/10	1	2.5	75
Paraffined.....	1 cc. M/10	2 cc. M/10	1 cc. M/100	1 cc. M/100	1	8.6	14
Paraffined.....	1 cc. M/10	2 cc. M/10	1 cc. M/100	2 cc. M/100	1	9.0	26
Glass at 25°C. (trans- parent).....	1 cc. M/10	2 cc. M/10	1 cc. M/10	1 cc. M/10	1	1.3	<1
Glass at 25°C. (trans- parent).....	1 cc. M/10	2 cc. M/10	1 cc. M/10	2 cc. M/10	1	1.3	5.8
Glass at 25°C. (trans- parent).....	2.5 cc. M/100	5 cc. M/100	2.5 cc. M/100	2.5 cc. M/100	1	2.7	<1
Glass at 25°C. (trans- parent).....	2.5 cc. M/100	5 cc. M/100	2.5 cc. M/100	5 cc. M/100	1	2.7	9.5

period only traces of hydrogen peroxide are decomposed. The occurrence of an induction period has been observed in the catalytic decomposition of hydrogen peroxide by ferric citrate, but no satisfactory explanation of this phenomenon

⁴As may be seen from table 4 and figure 3, an induction period may be observed at very low cupric citrate concentrations even when the $\text{Cu}^{++}:\text{Na}_3\text{Ci}$ ratio is 1:1, and also at very low concentration of sodium tungstate or sodium molybdate (M/20,000).

has been advanced (8). A detailed investigation of the character of the induction period was carried out. The results of these experiments, which are presented in table 5, have led to the following conclusions:

(1) The induction period is markedly dependent on the surface area of the reaction vessel. In otherwise equal conditions it is eight to ten times longer in glass vessels than in paraffined vessels. The nature of the wall of the reaction vessel affects the induction period but not the reaction velocity.

(2) The induction period is also influenced by light. In glass vessels which were varnished on the outside with a black varnish, the induction period was shorter than in similar vessels which had not been protected from light; light exerted no appreciable influence on the reaction velocity.

(3) The length of the induction period decreases as the temperature is increased. The reaction velocity varies positively with temperature.

(4) The length of the induction period is predominantly dependent on the concentration of the free cupric ion in the solution. It is prolonged if its concentration is decreased. The concentration of free cupric ion depends on the absolute concentration of cupric citrate complex as well as on the molar ratio of $\text{Cu}^{++}:\text{Na}_3\text{Ci}$. The composition of the complex conforms to the ratio of $\text{Cu}^{++}:\text{Na}_3\text{Ci}$ as 1:1. Evidence for the formation of this complex in solution can easily be produced from conductometric titration, where a break at the ratio 1 $\text{Cu}:1\text{Na}_3\text{Ci}$ is obtained. As long as the relationship $\text{Na}_3\text{Ci}:\text{Cu}$ is not greater than 1, no appreciable induction period occurs at adequate absolute concentration of cupric ion, but an excess of trisodium citrate strongly decreases the dissociation of the complex and thus leads to a prolongation of the induction period. The following differences in behavior between cupric citrate and ferric citrate show the relation between the occurrence of the induction period and the nature of the complex present: An induction period occurs in the presence of an excess of trisodium citrate if the ratio $\text{Na}_3\text{Ci}:\text{Cu}^{++}$ is greater than 1. This is in accordance with the 1:1 ratio of the composition of the cupric citrate complex. In the presence of ferric citrate two complexes are formed; one labile, conforming to the composition $\text{Fe}^{+++}:\text{Na}_3\text{Ci} = 3:2$; one stable, conforming to the composition $\text{Fe}^{+++}:\text{Na}_3\text{Ci} = 2:3$ (3). It was found that the induction period becomes noticeable in fact in the presence of ferric citrate when the ratio $\text{Fe}^{+++}:\text{Na}_3\text{Ci}$ is as 3:2. When the ratio $\text{Fe}^{+++}:\text{Na}_3\text{Ci}$ is as 2:3, the catalytic decomposition of hydrogen peroxide is virtually nil.

Only negligible quantitative differences between the induction period observed in the presence of sodium tungstate and sodium molybdate, respectively, were found. In table 5, therefore, only data for sodium tungstate are presented. The induction period is in no way affected if one of the following rather than hydrogen peroxide is added to the reaction mixture as the last component:

- (1) Na_2WO_4 (or Na_2MoO_4)
- (2) Na_2WO_4 (or Na_2MoO_4) + CH_3COOH
- (3) $\text{Cu}(\text{NO}_3)_2$
- (4) $\text{Cu}(\text{NO}_3)_2$ + Na_3Ci

When a further portion of hydrogen peroxide is added to a reaction mixture in which decomposition has already occurred, no second induction period is observed, independently of whether the first decomposition was or was not preceded by an induction period. A second induction period occurs, however, if sodium citrate in excess is added to the mixture together with the second portion of hydrogen peroxide. The explanation of these observations will be considered in the discussion.

TABLE 6

Absorption spectrum of the blue complex (present before decomposition) and of the green complex (present after decomposition)

- (1) 0.5 cc. 1 *M* Na₂WO₄ + 1 cc. 1 *M* CH₃COOH + 0.5 cc. 1 *M* Cu(NO₃)₂ + 0.5 cc. 1 *M* Na₃Ci + 10 cc. H₂O
 (2) 0.5 cc. 1 *M* Na₂WO₄ + 1 cc. 1 *M* CH₃COOH + 0.5 cc. 1 *M* Cu(NO₃)₂ + 0.5 cc. 1 *M* Na₃Ci + 5.0 cc. 1 *M* H₂O₂ + 5 cc. H₂O

Measurements were carried out 1 hr. after the decomposition

SPECTRAL REGIONS	EXTINCTION ($\log_{10} I_0/I$) IN A SOLUTION LAYER OF 5 MM.	
	1 (Blue).	2 (Green)
<i>mμ</i>		
690	0.770	0.690
660	0.498	0.430
570	0.180	0.205
550	0.045	0.165
530	0.040	0.185
500	0.035	0.240
470	0.028	0.365
450	0.025	0.460

THE CATALYTICALLY ACTIVE COMPOUND FORMED FROM THE CITRATE COMPLEX IN THE INITIAL STAGES OF THE CATALYSIS

The following experiments show that the catalytically active substance is not the original citrate complex itself, but a new substance which is derived from the citrate complex.

A. Results of photometric experiments

During the catalytic decomposition of hydrogen peroxide by sodium tungstate or sodium molybdate in the presence of cupric citrate, the blue color of the solution which is due to the presence of the cupric citrate complex becomes green in an early stage of the catalytic process. The color transition was further investigated photometrically. The experiments were carried out with a Hellige panphotometer. Extinction was measured in a solution layer of 5 mm. at a temperature of 18°C. Table 6 shows the absorption spectrum of the blue cupric citrate complex (before decomposition) and of the green complex (after decomposition). The intensity of the color is independent of the concentration of tungstate or molybdate and the color density is the same whether sodium tungstate or so-

dium molybdate is used. This applies to the blue cupric citrate complex as well as to the green complex formed during the process of the decomposition. It was found, on the other hand, that the presence of a threshold quantity of hydrogen peroxide is essential for the conversion of the cupric citrate complex. Figure 4 shows the absorption characteristics of the newly formed complex in the spectral region of 470 $m\mu$ and 450 $m\mu$ as a function of the initial molar relation of hydrogen peroxide to the cupric citrate complex. In the spectral regions of 470 $m\mu$ and 450 $m\mu$ the absorption of the blue complex is very small in comparison to that of the green complex (see table 6).

The curves presented in figure 4 show clearly that two molecules of hydrogen peroxide must be present per molecule of cupric citrate in order that the catalytically active new complex may be formed in a quantitative yield.

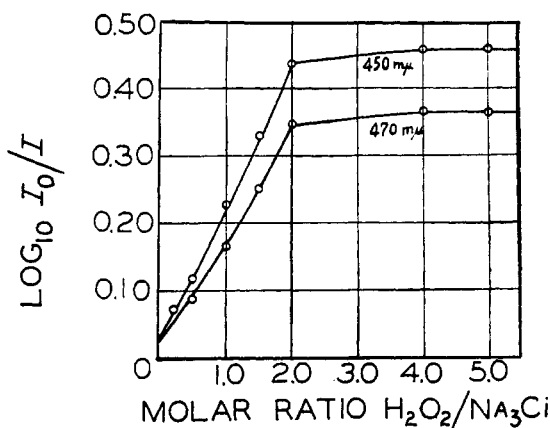


FIG. 4. The absorption characteristics of the cupric citrate complexes. Composition of reaction mixtures: 0.5 cc. 1 M Na_2WO_4 + 1 cc. 1 M CH_3COOH + 0.5 cc. 1 M $Cu(NO_3)_2$ + 0.5 cc. 1 M Na_3Ci + x cc. 1 M H_2O_2 + $(10 - x)$ cc. H_2O .

The new complex, like the original cupric citrate complex, contains the cupric ion and an anion derived from citrate in a ratio of 1:1, since in both cases an excess of citrate added at the beginning of the reaction (corresponding to a ratio greater than 1:1) exerts only a small influence on the color density. It may be noted that in experiments in which an induction period occurs, no change in color takes place during the induction period.

B. Results of conductometric experiments

In order to obtain further information concerning the complexes or intermolecular compounds which occur in the system Na_2WO_4 (or Na_2MoO_4) + CH_3COOH + $Cu(NO_3)_2$ + Na_3Ci , conductometric titrations were undertaken. The conductometric measurements were carried out with the aid of a lyograph produced by Lautenschläger (4). The reaction mixtures were composed as follows:

- (A) 1 cc. 1 M Na_2WO_4 + 2 cc. 1 M CH_3COOH + 1 cc. 1 M $Cu(NO_3)_2$ + 46 cc. H_2O (in the conductometric cell). Titration against 1 M trisodium citrate with a microburet.

- (B) 1 cc. 1 M Na_2WO_4 + 49 cc. H_2O (in the conductometric cell). Titration against 1 M trisodium citrate.
 (C) 1 cc. 1 M Na_2WO_4 + 2 cc. 1 M CH_3COOH + 47 cc. H_2O (in the conductometric cell). Titration against 1 M trisodium citrate.
 (D) 1 cc. 1 M $\text{Cu}(\text{NO}_3)_2$ + 49 cc. H_2O (in the conductometric cell). Titration against 1 M trisodium citrate.
 (E) 1 cc. 1 M Na_2WO_4 + 2 cc. 1 M CH_3COOH + 47 cc. H_2O (in the conductometric cell). Titration against 1 M cupric nitrate.

All experiments were carried out at 25°C. At each titration, aliquots of 2.5 cc. were run from the microburet into the solution. The conductometric curves showed a definite inflection only in experiments A and D at $\text{Cu}^{++}:\text{Na}_3\text{Ci}$ ratios of 1:1. This shows that a cupric citrate complex conforming to the ratio 1:1 is

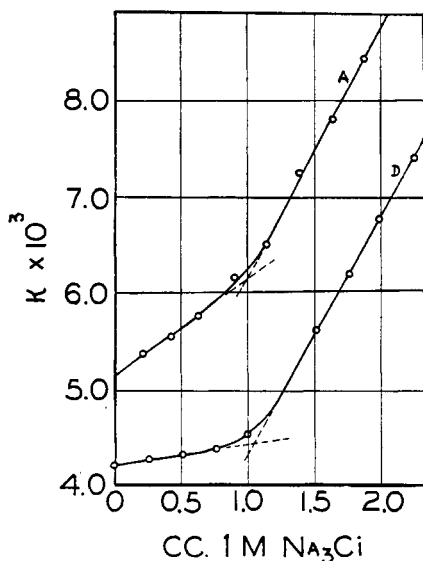


FIG. 5. Conductometric titrations. Composition of experiments given in the text. κ = specific conductivity.

the only complex present in the system in question (the conductometric curves obtained in experiments A and D are presented in figure 5). No complex formation occurs between tungstate and citrate, in contrast to the behavior of tartrate.⁵ Neither is a complex formed between tungstate and cupric ion. Analogous experiments carried out with sodium molybdate in the place of sodium tungstate led to the same conclusions, *viz.*, that the only complex present in the system is cupric citrate and that no complex formation between citrate and molybdate occurs.

The conductivity of the solutions in the course of the reaction was measured. Table 7 gives the results of two experiments: (1) a decomposition which was not preceded by an induction period; (2) a decomposition preceded by an induction period. The results presented in table 7 show that the variations in conductivity are relatively small and do not exceed 3 per cent. This shows that the complex

which is formed in the course of the catalytic process contains cupric ion and the organic anion in the 1:1 ratio of the original citrate complex; otherwise large differences in conductivity should have been observed. This conclusion is consistent with the findings of the photometric experiments. Conductometric experiments with sodium molybdate mixtures gave results analogous to those obtained with sodium tungstate.

C. Results of measurements of the evolution of carbon dioxide

Qualitative tests revealed that both carbon dioxide and oxygen are evolved during the catalytic decomposition of hydrogen peroxide by sodium tungstate (or sodium molybdate) in the presence of cupric citrate in a slightly acid solution.

TABLE 7

Variation in specific conductivity of the reaction mixtures during the decomposition (at 25°C.)

- (1) 1 cc. $M/10$ Na_2WO_4 + 2 cc. $M/10$ CH_3COOH + 1 cc. $M/10$ $\text{Cu}(\text{NO}_3)_2$ + 1 cc. $M/10$ Na_3Ci + 44 cc. H_2O + 1 cc. 2 M H_2O_2 (added at zero time)
 (2) 1 cc. $M/10$ Na_2WO_4 + 2 cc. $M/10$ CH_3COOH + 1 cc. $M/10$ $\text{Cu}(\text{NO}_3)_2$ + 2 cc. $M/10$ Na_3Ci + 43 cc. H_2O + 1 cc. 2 M H_2O_2 (added at zero time)

(1)		(2)	
TIME	$\kappa \times 10^3$	TIME	$\kappa \times 10^3$
<i>min.</i>		<i>min.</i>	
0	1.028	0	1.350
0.25	1.000	0.25	1.320
1	1.005	1	1.318
2	1.010	2	1.320
4	1.020	4	1.322
6	1.026	6	1.325
8	1.030	8	1.320
10	1.035	10	1.315
15	1.035	15	1.310
25	1.035	25	1.310
35	1.035	35	1.310

Nevertheless the total volume of gas evolved is equivalent to the theoretical expectation for active oxygen from hydrogen peroxide. This fact suggests that an equimolecular amount of oxygen replaces the deficit of carbon dioxide (i.e., two atoms of oxygen replace one molecule of carbon dioxide) in the catalytically active complex which is formed from citrate. Permanganimetric experiments described in a succeeding section confirm this interpretation. The findings in systems containing ferric citrate and cobalt citrate were similar and further support the same assumption. It seems likely that a revision of the conclusions drawn in earlier work on the catalytic decomposition of hydrogen peroxide by citrate complexes (5, 8) will be made necessary by this finding. *In all these cases it is not the original citrate but a new complex formed from citrate which is the active catalyst.* Determinations of the amount of the evolved carbon dioxide were car-

ried out with an apparatus which consisted of six wash bottles connected in series to a water-jet vacuum pump. The first two bottles in the series contained solutions of sodium hydroxide, which absorbed carbon dioxide from the atmosphere. The third bottle was the reaction vessel and was kept in a thermostat at a temperature of $15^{\circ}\text{C}.$ ($\pm 0.1^{\circ}$). The last three bottles contained the absorption solution, i.e., 50 cc. of a clear 0.1 M solution of barium hydroxide whose concentration was tested before each experiment by titration against 0.2 N nitric acid, using phenolphthalein as indicator.⁵ In the course of the decomposition a precipitate of barium carbonate appeared in the absorption solution.⁶ A stream of air was passed through the system at a rate of about three bubbles per second throughout the course of the experiments, and for 10 min. afterwards. At the end of this time 10 cc. of 1 N barium chloride was added to each of the three flasks and the suspension was titrated against 0.2 N nitric acid. It is known that a suspension of barium carbonate in the presence of an excess of barium ion is acid to phenolphthalein, a circumstance which makes it possible to use this indicator for titrations of excess barium hydroxide. The total difference between the first and last titrations of the three flasks permitted calculation of the amount of evolved carbon dioxide.

The reaction mixtures were composed as follows: x cc. 1 M Na_2WO_4 (or Na_2MoO_4) + $2x$ cc. 1 M CH_3COOH + y cc. 1 M $\text{Cu}(\text{NO}_3)_2$ + z cc. 1 M Na_3Ci + r cc. 2 M H_2O_2 + $(20 - 3x - y - z - r)$ cc. H_2O .

The results of the measurements may be summarized as follows:

(a) Where the molar ratio $\text{H}_2\text{O}_2:\text{Na}_3\text{Ci}$ is greater than 2:1, one mole of carbon dioxide is evolved per mole of sodium citrate in the reaction mixture, independently of the concentration of tungstate or molybdate or of the ratio $\text{Cu}^{++}:\text{Na}_3\text{Ci}$ (the experiments were carried out within a molar range of $\text{Cu}^{++}:\text{Na}_3\text{Ci}$ as 10:1 to 1:2). Where the decomposition was preceded by an induction period, no carbon dioxide was evolved during this period.

(b) Where the molar ratio $\text{H}_2\text{O}_2:\text{Na}_3\text{Ci}$ was less than 2:1, half a mole of carbon dioxide was evolved per mole of hydrogen peroxide decomposed.

The above findings show once more that at least two molecules of hydrogen peroxide combine with one molecule of citrate in the quantitative formation of the new complex and, furthermore, that two molecules of hydrogen peroxide can supply the two atoms of oxygen which enter into this complex in the place of the evolved molecule of carbon dioxide.

D. Results of permanganimetric titrations

In order to measure the consumption of potassium permanganate by the original citrate complex and by the new complex formed during the course of the catalysis, titrations according to Kolthoff (9) were performed. An excess of potassium permanganate was added to the solutions and reduction was allowed

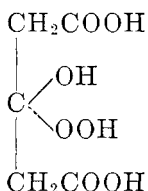
⁵ Since the second titration for the determination of the remaining barium hydroxide must be carried out against phenolphthalein, better results are obtained if the first titration is carried out with phenolphthalein rather than methyl orange as indicator.

⁶ The solution in the third bottle should be only faintly turbid.

to proceed in the alkaline solution for 24 hr. at room temperature. After acidification, the excess of potassium permanganate was titrated against oxalic acid (for details see *loc. cit.*). The titrations showed that the original citrate in conformity to its chemical formula consumes nine atoms of oxygen per molecule, i.e., 1 cc. of 1 *M* trisodium citrate is equivalent to 18 cc. of 1 *N* potassium permanganate. The newly formed complex, on the other hand, consumes seven atoms of oxygen per molecule of complex, i.e., 1 cc. of a molar solution of the new complex is equivalent to 14 cc. of 1 *N* potassium permanganate. This leads to the conclusion that two atoms of oxygen enter the complex during the process of decomposition of hydrogen peroxide. It may be noted, further, that the new complex is destroyed by potassium permanganate much more rapidly than is the original citrate complex. The kinetic experiments showed further that the oxidation of the new complex by potassium permanganate is a stepwise one. Five atoms of oxygen are absorbed by the new complex with a velocity which is approximately 200 times greater than is the velocity of oxygen absorption by the original citrate complex in similar conditions. The absorption of the final two atoms of oxygen, on the other hand, is slow. Formic acid, which was identified by its specific odor, was found to be an intermediary of the oxidation.

E. Structure of the active complex

It is supposed that the catalytically active complex formed in the first stage of the process of decomposition is a complex compound of cupric ion with the sodium salt of the following acid:

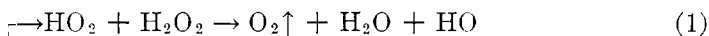


The following experimental findings support the assumed structure: Measurements of the amount of carbon dioxide evolved show that one mole of carbon dioxide is evolved per mole of sodium citrate present in the presence of an excess of hydrogen peroxide, the molar ratio $\text{H}_2\text{O}_2:\text{Na}_3\text{Ci}$ being greater than 2:1. Since only one mole of carbon dioxide is evolved, it must be assumed that it derives from the most labile carboxyl group of the citric acid molecule, i.e., from the carboxyl adjacent to the hydroxyl group. Otherwise, evolution of two moles of carbon dioxide per mole of citrate would have to be expected. The gasometric experiments which were carried out in acid solution show that the amount of gas evolved is the equivalent of the active oxygen content of hydrogen peroxide. This must mean that two atoms of oxygen enter the complex in the place of one evolved mole of carbon dioxide. The permanganimetric titrations confirm this conclusion, as under any other assumption it would not be comprehensible why seven atoms of oxygen rather than nine have to be consumed per mole of citrate in order that quantitative destruction of the complex may be realized. The step-

wise reduction of potassium permanganate by the new compound is smoothly compatible with the proposed structure. It may be assumed that the first five oxygen atoms absorbed split the complex oxidatively into two molecules of formic acid and that the latter are then oxidized by potassium permanganate only slowly. The photometric experiments confirm that the two moles of hydrogen peroxide are consumed per mole of original citrate complex present where quantitative conversion into the new compound takes place. The very small variation in the conductivity of the reaction solution from the beginning of the decomposition to its end supports the view that no fundamental changes occur in the general structure of the citrate molecule, which is that of a tribasic acid with a hydroxyl group adjacent to the middle carbon. The only probable explanation is that two atoms of oxygen replace one mole of carbon dioxide in the complex, with the result that a —COOH group is replaced by —O—O—H .

Discussion

Haber and Weiss (6) came to the conclusion that the catalytic decomposition of hydrogen peroxide by ferric ion is a chain reaction in which the free radicals HO_2 and HO participate according to the following scheme:



Certain reactions lead to an initiation of the chain. With Fe^{+++} the initiating reaction is:



(as hydrogen peroxide is a weak acid and the anion HO_2^- exists in its solution). Similarly, in the case of cupric ion the following reaction initiates the chain:



Certain reactions can break the chain. These are mostly the reverse processes of reactions which initiate the chain, e.g., reactions 3 and 4 in the leftward direction. The reason why the simple cations Fe^{+++} and in particular Cu^{++} fail to exert a powerful catalytic effect on the decomposition of hydrogen peroxide lies in the fact that in this case the initiating reactions 3 and 4 reach an equilibrium at a point in which the leftward direction of the reaction is favored, i.e., the chain-breaking reaction predominates.

The assumption of a chain mechanism accounts for all the experimental data so far obtained and seems to the author to be the only hypothesis which can explain the existence of an induction period and the other peculiarities of the influence of citrate.

The promoter effect of cupric ion in the presence of tungstate or molybdate can be explained by the assumption that in this case the free radicals HWO_6 (HMoO_6) and HWO_5 (HMoO_5) are carriers of the chain, and that the chain-initiating reaction is mediated by the anion HWO_6^- or HMoO_6^- (which is present in the solution at the pH of the experiments, according to K. F. Jahr (7)) rather than

by the anion HO_2^- . In this connection it is worth noting that pertungstic acid and permolybdic acid are far stronger acids than hydrogen peroxide, whose constant of dissociation at 20°C. for the first hydrogen ion is $K_1 = \sim 10^{-12}$, and that the concentration of HWO_6^- or HMoO_6^- ion is far greater than is the concentration of HO_2^- ion. The reaction mechanism may be represented as follows:



The reaction with molybdate is an analogous one. The promoter effect may be explained in this case by the circumstance that the equilibrium point of the chain-initiating reaction lies more to the right than is the case in reaction 4 with HO_2^- . As has been shown by Bobtelsky and Kirson (2), the cupric chloro-complex is a far stronger catalyst for the decomposition of hydrogen peroxide than the simple cupric ion. This fact as well may be explained on the assumptions which have been put forward. The equilibrium 4 is shifted to the right in the presence of concentrated chloride solution (sodium chloride, potassium chloride, or ammonium chloride), since the chloro-complex of cuprous ion is far more stable in comparison to the chloro-complex of cupric ion than is simple cuprous ion in comparison to simple cupric ion. It may now readily be comprehended why the chloro-complex of cupric ion acts as a promoter in the presence of tungstate or molybdate also in a weakly acid solution (at a pH of 4.5–5), i.e., in conditions in which it does not act directly on hydrogen peroxide. Hydrogen peroxide is a very weak acid and the concentration of hydrogen ion in the reaction mixture at pH 4.5–5.0 suffices to diminish the dissociation of hydrogen peroxide considerably. Consequently, the concentration of the anion HO_2^- is decreased to such an extent that the chain-initiating reaction (reaction 4) for which HO_2^- ions are necessary is practically abolished. On the other hand, the pH of the solutions does not exert an effect of similar magnitude on the dissociation of H_2WO_6 or H_2MoO_6 (at least insofar as the dissociation of the first hydrogen ion is concerned), and in consequence the concentration of the ions HWO_6^- or HMoO_6^- is not noticeably affected by the pH of the reaction mixture. For this reason the chloro-complex of copper is a weak catalyst for the decomposition of hydrogen peroxide at pH 4.5–5.0 but is an active promoter (additional catalyst) in the presence of tungstate or molybdate at the same pH.

It follows from the assumptions which have been made above that stable complexes such as the cyanide complex of copper cannot be active catalysts of the decomposition of hydrogen peroxide, since the removal of the entire store of cupric ion and its transformation into a stable complex renders the chain-initiating reaction (reaction 4) impossible.

The activity of citrate complexes is explicable on these assumptions. The existence of an induction period is known in many chain reactions and its very existence with reference to the action of citrates in the conditions which have been

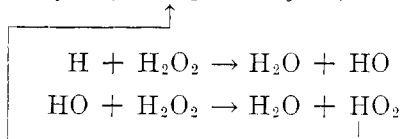
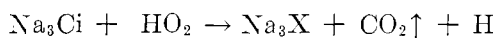
described is evidence of the chain character of the reaction. It is to be assumed that not only the decomposition itself but the actual formation of the active catalyst is a chain reaction.

The influence of ferric citrate on the decomposition of hydrogen peroxide has been investigated by Bobtelsky and Kirson (8). In the present study of the action of cupric citrate it has been shown that the action of this salt is analogous in many respects to that of the iron salt. There are, however, two fundamental divergencies:⁷

(a) Ferric citrate acts directly on hydrogen peroxide. Cupric citrate does not act directly on hydrogen peroxide and is only active in the presence of tungstate or molybdate. The reason for this difference in behavior lies in the fact that the chain-initiating reaction is a reduction which is accomplished more easily with trivalent iron than with divalent copper; it is significant that trivalent iron acts on hydrogen peroxide even in a weakly acid solution containing minimal concentrations of HO_2^- ion.

(b) The first appearance of the induction period. This occurs in the two cases at different ratios of citrate and metal. This finding is explained by the fact that different complexes are formed in the two cases. In the case of copper the complex is composed of cupric ion and trisodium citrate in a ratio 1:1, whereas in the case of iron two complexes are formed, one labile with a composition corresponding to $\text{Fe}^{+++}:\text{Na}_3\text{Ci}$ as 3:2, and a second stable, with a composition corresponding to $\text{Fe}^{+++}:\text{Na}_3\text{Ci}$ as 2:3 (3). The relation of the composition of the complexes to the term of the induction period is further explained below.

The chain-initiating reaction with respect to citrate activity may be assumed to conform to the mechanism which has been proposed in the presence of both copper and iron. As long as citrate is present in the solution, the formation of the new complex, the structure of which has been discussed in the foregoing, proceeds by oxidation according to the following mechanism (Na_3X represents the sodium salt of the new acid):



The oxidation mechanism in the presence of tungstic or molybdic acid is assumed to be analogous, involving HWO_6 (or HMoO_6) radicals instead of HO_2 . The active catalyst is a complex of cupric ion with Na_3X at a ratio of 1:1. The mechanism of the catalysis conforms to the activity of a labile complex such as the chloro-complex.

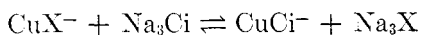
The explanation of the induction period may now be considered. When the concentration of free cupric or ferric ions is reduced below certain limits, the

⁷The behavior of cobaltous citrate requires separate investigation, in view of the results here reported.

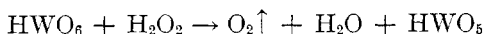
chain-initiating reaction becomes so rare that most of the free radicals which are formed disappear by recombination on the surfaces of the reaction vessel. In this case a measurable period of time must elapse before the chain-initiating reactions become effective. This is the case when the ratio $\text{Na}_3\text{Ci}:\text{Cu}^{++}$ exceeds 1.0 (when a complex is formed) or when the concentration of added copper is small in the absolute sense. An induction period also occurs in mixtures containing very low concentrations of tungstate or molybdate, since the ions HWO_6^- (or HMoO_6^-) participate in the chain-initiating reaction. In the case of ferric citrate the induction period occurs when the relation $\text{Fe}^{+++}:\text{Na}_3\text{Ci}$ reaches 3:2, since at this ratio a labile complex of appreciable dissociation is formed. The catalytic decomposition is practically brought to an end when the ratio $\text{Fe}^{+++}:\text{Na}_3\text{Ci}$ is increased to 2:3, since the stable complex formed in a reaction mixture with this ratio has a dissociation so small that the chain-initiating reaction virtually ceases to exist. The relation of the term of the induction period to the composition of the complex is thus comprehensible.

It may be assumed that the recombination of the free radicals occurs on the surface of glass more easily than on paraffin. The induction period is therefore longer in glass vessels than in paraffined vessels. Otherwise the marked dependence of the term of the induction period on the character of the surface of the reaction vessel is incomprehensible. Light appears to initiate a reaction by which free radicals disappear, since the term of the induction period is longer in light than in dark. The exact meaning of this effect is not yet understood. Increase in the temperature raises the velocity of the chain-initiating reaction and brings about an increase in the concentration of free cupric ions by increasing the dissociation of the complex. In consequence the term of the induction period is curtailed with increase in temperature.

It is obvious that an induction period does not precede the decomposition of a newly added portion of hydrogen peroxide, since the necessary catalyst is already present in this case in the reaction mixture at the time of the addition of the second portion of hydrogen peroxide. A new addition of an excess of sodium citrate to the reaction mixture, however, exerts an inhibitory effect on the decomposition because of the equilibrium:



The monomolecular course of the catalytic decomposition of hydrogen peroxide in the presence of tungstate or molybdate can be explained on the above view. In the presence of tungstate or molybdate the pace-setting reaction is the following:



The concentration of HWO_6 , according to reaction 5, is proportional to the concentration of HWO_5^- and is independent of the concentration of hydrogen peroxide, since the pertungstic acid is formed in quantitative yield immediately following the addition of hydrogen peroxide in a large excess. Consequently the catalytic reaction follows the course of a first-order reaction with reference to the concentration of hydrogen peroxide.

The failure of the speed of decomposition of hydrogen peroxide to vary linearly either with the concentration of tungstate or molybdate or with the concentration of copper citrate may be explained if it is assumed that recombination of the free radicals HWO_2 (or HMoO_2) in the reaction mixture is favored by increase of their concentration.

The chain reaction mechanism thus appears to offer an explanation for varied peculiarities of the process of the catalytic decomposition of hydrogen peroxide, since the pertungstic acid is formed in quantitative yield immediately the occurrence of an induction period, and various by-effects of the latter. Recently Baxendale, Evans, and Park (1) have applied part of the Haber and Weiss scheme to polymerization phenomena in aqueous solution in the presence of hydrogen peroxide. Weiss (11) has also assumed the action of enzymes, such as catalase and peroxidase, to be based on the same fundamental principles. It has been attempted to substitute the HO_2 radical by the O_2^- ion. In view of recent calculations however on the bond strengths involved in the HO_2 radical this, once again, is considered as dubious. In this paper, therefore, the undissociated radicals have been applied throughout.

SUMMARY

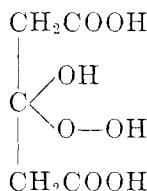
1. The catalytic decomposition of hydrogen peroxide by sodium tungstate and sodium molybdate was investigated in the presence of simple cations at a pH of 5-6. Among the cations which were investigated (Cu^{++} , Co^{++} , Ni^{++} , Mn^{++} , Cd^{++} , Zn^{++}) the most active was cupric ion. The catalytic decomposition was always of the first order.

2. The action of the simple cations is increased in the presence of a concentrated chloride solution. The cupric chloro-complex shows forty times greater activity than the simple cupric ion. The chloro-complex is an effective additional catalyst in the presence of molybdate or tungstate even in slightly acid solution (pH = 4.5-5), in which it does not act on hydrogen peroxide directly.

3. The complex of cupric citrate does not itself act on hydrogen peroxide but is an active additional catalyst in the presence of tungstate or molybdate ions. The activity of the cupric citrate complex is about ten times that of the simple cupric ion. The activity is due not to the original citrate complex but to a new compound which is formed in an early stage of the decomposition of hydrogen peroxide. The mechanism of the decomposition has been studied. Under certain conditions, the reaction curve showed an induction period lasting from a few minutes to some hours. It existed when the concentration of free cupric ion or of tungstate or molybdate was very small. The concentration of the free cupric ion depends on the absolute concentration of the cupric citrate complex as well as on the ratio of cupric ion to sodium citrate. The induction period is influenced by the nature of the wall surface of the reaction vessel, light, and temperature.

4. The structure and properties of the active compound formed in an early phase of the catalytic process have been investigated. For each mole of citrate present in a solution containing an excess of hydrogen peroxide, one mole of carbon dioxide is set free and is replaced in the citrate complex by two atoms of

oxygen. The blue color of the solution changes to green. There are only slight concomitant changes in the conductivity of the solution. The quantitative oxidation of the active compound involves two atoms less of oxygen than does the oxidation of the original citrate complex. The structure of the active compound is assumed to be that of copper with the anion of the following acid:



Aci-form of the perhydrate of acetonedicarboxylic acid

5. It is suggested, in harmony with the conclusions of F. Haber and J. Weiss, that the mechanism of the decomposition of hydrogen peroxide is a chain reaction involving free radicals.

The assumed mechanism explains the following facts:

- (a) The promoting action of cupric ion in the presence of tungstates and molybdates.
- (b) The greater activity as a catalyst and promoter of cupric complex in comparison with simple cupric ion.
- (c) The fact that the cupric chloro-complex does not act directly on hydrogen peroxide in a slightly acid solution ($\text{pH} = 4.5-5$) but is active in the presence of tungstate or molybdate ions under the same conditions.
- (d) The action of the complex citrates of cupric ion and ferric ion, including the formation of the catalytically active compound.
- (e) The course of the reaction and the phenomenon of the induction period preceding hydrogen peroxide decomposition.

6. In free-radical gas-phase reactions the dependence of an induction period on the nature of the wall surface has been frequently observed. This is the first time to our knowledge that this phenomenon has been observed in the liquid phase. This may be considered as supporting evidence for the view first put forward by Haber and Weiss that free radicals take part in the catalytic decomposition of hydrogen peroxide in homogeneous solution.

REFERENCES

- (1) BAXENDALE, J. H., EVANS, M. G., AND PARK, G. S.: *Trans. Faraday Soc.* **42**, 155 (1946).
- (2) BOBTELSKY, M., AND KIRSON, B.: *Compt. rend.* **199**, 573 (1934).
- (3) BOBTELSKY, M., AND SIMCHEN, A. E.: *Compt. rend.* **208**, 1646 (1939).
- (4) BOBTELSKY, M., AND SIMCHEN, A. E.: *J. Am. Chem. Soc.* **64**, 454 (1942), for a description of the apparatus.
- (5) BOBTELSKY, M., AND SIMCHEN, A. E.: *J. Am. Chem. Soc.* **64**, 2492 (1942).
- (6) HABER, F., AND WEISS, J.: *Proc. Roy. Soc. (London)* **A147**, 332 (1934); *Naturwissenschaften* **20**, 948 (1932).
- (7) JAHR, K. F.: *Ber. Ges. Freunden tech. Hochschule Berlin* **1939**, 91-3; *Chem. Abstracts* **36**, 6933 (1942).

- (8) KIRSON, B.: Thesis, University of Jerusalem, 1939.
BOBTELSKY, M., AND KIRSON, B.: Compt. rend. **208**, 1577 (1939).
- (9) KOLTHOFF, I. M.: *Die Massanalyse*, Vol. II, p. 356. J. Springer, Berlin (1931).
- (10) ROBERTSON, A. C.: J. Am. Chem. Soc. **47**, 1299 (1925); **48**, 2072 (1926); **49**, 1630 (1927).
BOHNSON, V. L., AND ROBERTSON, A. C.: J. Am. Chem. Soc. **45**, 2512 (1923).
- (11) WEISS, J.: J. Phys. Chem. **41**, 1107 (1937).

DISTRIBUTION LAW, ADSORPTION, AND CHEMICAL REACTION. II

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INTRODUCTION

In a previous paper (12) the author has tried to show that if adsorption is regarded as a special case of distribution of a substance between two phases the phenomena of distribution, adsorption, and chemical reaction appear to have a simple correlation. The special feature of the distribution is that the dimensions of the adsorbing phase are regarded as limited. The illustrations in support of this view adduced in that paper have been somewhat of a qualitative character. It is proposed to show in this paper that some results of a general nature and some others of a rather strictly quantitative character are in harmony with this view.

SOME THEORETICAL CONSIDERATIONS REGARDING THE STATE OF
ADSORBED MOLECULES

The adsorption equation of Langmuir (20) and similar equations have been deduced by assuming highly simplified conditions for adsorption. It is therefore quite easily understood that some of the equations have little utility in explaining the experimentally determined courses of adsorption isotherms. One of the simplified conditions is that the adsorbed molecules be confined to a homogeneous two-dimensional space. Such a condition is probably difficult to realize when the adsorbent is a solid. There are bound to be edges, cracks, corners, or boundaries between two or more solid phases, and other factors against the exclusive existence of a homogeneous plane surface. Probably all the theories of adsorption so far regard the adsorbed substance as being present in a more or less homogeneous condition, e.g., a homogeneous gas or a liquid, sometimes with continuous pressure or density gradients from point to point.

There are a number of theoretical considerations against these simple views. To call attention to a simple point, reference may be made to the fundamental equation of capillarity (1):

$$P_0 - P = \left(\frac{1}{R_1} + \frac{1}{R_2} \right) (\sigma_0 - \sigma)$$