THE MECHANISM OF REACTIONS IN AQUEOUS SOLUTION

EXAMPLES INVOLVING EQUILIBRIA AND STEADY STATES

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It is generally recognized by chemists that many homogeneous reactions take place in steps, and that the order of a reaction, determined by rate measurements, designates the molecules that react in or before the rate-determining step. However, there is undoubtedly much scepticism about the possibility of identifying the intermediate compounds formed in and after the rate-determining reaction. The purpose of the author in this review is to illustrate the study of the mechanism of reactions in aqueous solutions by means of examples; in some of these the identification of the intermediate compounds seems to be so complete that the mechanism may be accepted as "proved."

Two examples will be discussed in some detail: one deals with the direct and the reverse reaction of a true equilibrium, the other with two reactions that lead to a steady state in the catalytic decomposition of hydrogen peroxide. The behavior of other catalysts for this decomposition will also be briefly considered, though in some cases the problem of the mechanism has not been solved.

In the presentation of this material, many details—which may be found in the original papers—will be omitted, such as the descriptions of analytical or other experimental methods. Also the effect on rates of variations in ionic strength will not be described; this subject is discussed under the heading "Kinetic salt effect" in a recent article by Livingston (1) entitled "An Introduction to Chemical Catalysis in Homogeneous Systems."
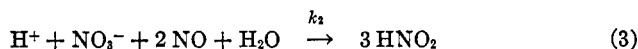
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REVERSIBLE REACTIONS

Abel and Schmid (2) have obtained the following results in aqueous solutions at 25°C. The rate of decomposition of nitrous acid

$$3\,HNO_2 \xrightarrow{k_1} H^+ + NO_3^- + 2\,NO + H_2O \qquad (1)$$
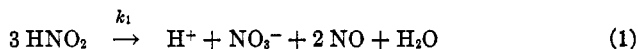
at a distance from the equilibrium obeys the law (2c)

$$-d(HNO_2)/dt = k_1(HNO_2)^4/(P_{NO})^2 \qquad (2)$$

The reverse reaction

$$H^+ + NO_3^- + 2\,NO + H_2O \xrightarrow{k_2} 3\,HNO_2 \qquad (3)$$

is autocatalytic, but its rate in the presence of nitrous acid is (2d)

$$+d(HNO_2)/dt = k_2(HNO_2)(H^+)(NO_3^-) \qquad (4)$$

It has also been shown (2f) that

$$k_1/k_2 = K \qquad (5)$$

the equilibrium constant of reaction 1, $(H^+)(NO_3^-)(P_{NO})^2/(HNO_2)^3$. The rate near the equilibrium is (2e)

$$-d(HNO_2)/dt = k_1(HNO_2)^4/P_{NO}^2 - k_2(HNO_2)(H^+)(NO_3^-) \qquad (6)$$

and equation 5 may be derived by setting this rate equal to zero. The constants have the following values (2f), corrected for salt effects, and based on the units moles per liter and minutes: at 25° $k_1 = 46$, $k_2 = 1.6$, $k_1/k_2 = 29$, $K = 29$.
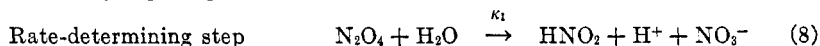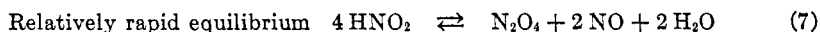
It seems worth while to consider at this point how such results as these are interpreted. Since only one term appears in each of the rate-equations 2 and 4, it is concluded that there is only one rate-determining step in each of the reactions 1 and 3. Any reaction which is assumed to precede a rate-determining reaction therefore must be reversible and have sufficient speed to insure maintenance of equilibrium. The experimental result
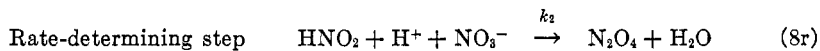
$$k_1/k_2 = K_{equilibrium}$$

has special significance since it proves that the two rate-determining steps are identical except in the matter of direction. The

immediate products of the rate-determining reaction, as well as the reacting substances, may thus be identified in this instance, since the products in one case are the reactants in the other. These conclusions are illustrated in the next paragraph.

The mechanism proposed by Abel and Schmid may be stated as follows:

Relatively rapid equilibrium $4\,HNO_2 \;\rightleftarrows\; N_2O_4 + 2\,NO + 2\,H_2O$ (7)

Rate-determining step $N_2O_4 + H_2O \;\xrightarrow{\;\kappa_1\;}\; HNO_2 + H^+ + NO_3^-$ (8)

The sum is reaction 1.

Rate-determining step $HNO_2 + H^+ + NO_3^- \;\xrightarrow{\;k_2\;}\; N_2O_4 + H_2O$ (8r)

Rapid follow reactions $N_2O_4 + 2\,NO + 2\,H_2O = 4\,HNO_2$ (7r)

The sum is reaction 3, the reverse of 1.

It is obvious that this mechanism agrees perfectly with the rate-equations 2, 4 and 6.   Thus it is an experimental fact (equation 2) that the rate of decomposition of nitrous acid is proportional to the concentration of N_2O_4; the assumption that the single rate-determining step is the reaction between N_2O_4 and water (equation 8) then follows directly.   The concentration of N_2O_4 in equilibrium with HNO_2 and NO gas was always extremely small, and the specific rate of reaction 8 is correspondingly large. This first order rate constant was calculated (2c) from the value of k_1 and an approximate value of the equilibrium constant of reaction 7.   At $25°\ \kappa_1 = 1 \times 10^7$.

The reason why very complicated results were obtained by the numerous investigators who had studied the rate of decomposition of nitrous acid is now clear: they allowed the pressure of NO gas to vary during their experiments.   The definite and relatively simple results of Abel and Schmid were obtained only by maintaining a constant pressure of NO gas during each run and preventing supersaturation.

The above results and mechanism are not in conflict with known facts, and will serve as a firm basis for future investigations of the chemistry of nitrogen compounds.   Thus it is well known that nearly pure nitrite is formed when the gases NO_2 and

N_2O_4 mixed with NO in excess are passed into an alkaline solution, even though in the absence of NO a mixture of nitrate and nitrite is formed apparently instantaneously. We have indeed the important generalization that the mixture of gases acts as the anhydride of nitrous acid more rapidly than N_2O_4 (or NO_2) alone can act as the mixed anhydride of nitric and nitrous acids. It should also be mentioned that Abel and his associates have recently demonstrated that the relation
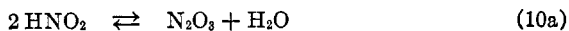
$$k_1/k_2 = K_{equilibrium}$$

holds at other temperatures (3), and that the very complex problem (2a) of the autocatalytic reduction of nitric acid to NO can be solved, at least when the reducing agent is arsenious acid (4).

While it is scarcely possible that any reasonable mechanism can be formulated which differs in principle from that shown in equations 7 and 8, nevertheless some possible changes in detail may well be considered. Since N_2O_4 is always in equilibrium with $2NO_2$, N_2O_4 in equations 7 and 8 could have been replaced by $2NO_2$. A decision between these two formulations seems impossible. It might be urged in favor of $N_2O_4 + H_2O$ in reaction 8 that the collisions involving two molecules are much more numerous than those with more than two; but this argument is not applicable in this instance since the water is always available when two molecules of NO_2 collide. However, this method of reasoning does apply in reaction 7; this, on account of its high order, undoubtedly takes place in steps. N_2O_3 is a probable intermediate compound, and has recently been proved to exist (5) in equilibrium with NO, NO_2 and N_2O_4. Its formation from the odd molecules NO and NO_2 is entirely analogous to the formation of N_2O_4 from $2NO_2$. Moreover, Abel, Schmid and Weiss (4) in their investigation of the reduction of nitric acid by arsenious acid have discovered a reaction involving $2HNO_2$ and $1H_3AsO_3$, and have assumed that N_2O_3 reacts in the rate-determining step

$$N_2O_3 + H_3AsO_3 \quad \rightarrow \quad 2NO + H_3AsO_4 \qquad (9)$$
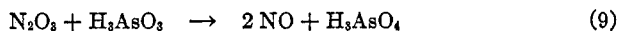
Reaction 7 may thus be replaced by the following set of reversible and extremely rapid reactions:

$$2\,HNO_2 \quad \rightleftharpoons \quad N_2O_3 + H_2O \qquad (10a)$$

$$N_2O_3 \quad \rightleftharpoons \quad NO_2 + NO \qquad (10b)$$

$$2\,NO_2 \quad \rightleftharpoons \quad N_2O_4 \qquad (10c)$$

Another example of a reversible reaction which takes place in steps, of which only one is rate-determining, is furnished by the reactions

$$H_3AsO_3 + I_3^- + H_2O \quad \underset{k_2}{\overset{k_1}{\rightleftharpoons}} \quad H_3AsO_4 + 2\,H^+ + 3\,I^- \qquad (11)$$
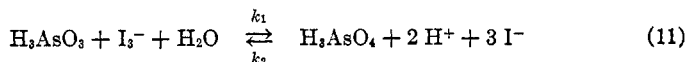
Many years ago Roebuck (6) demonstrated that

$$\frac{-\,d(H_3AsO_3)}{dt} = k_1 \frac{(H_3AsO_3)\,(I_3^-)}{(H^+)\,(I^-)^2} \qquad (12)$$

$$\frac{+\,d(H_3AsO_3)}{dt} = k_2\,(H_3AsO_4)\,(H^+)\,(I^-) \qquad (13)$$

and

$$k_1/k_2 = K_{\text{equilibrium}}$$

By means of data from Roebuck's first paper, Bray (6b) showed that as equilibrium is approached the rate is equal to the difference between the two rates 12 and 13. The only reasonable mechanism is that suggested by Roebuck:

Relatively rapid equilibria $\qquad\quad I_3^- \quad \rightleftharpoons \quad I_2 + I^- \qquad (14)$

$$I_2 + H_2O \quad \rightleftharpoons \quad HIO + H^+ + I^- \qquad (15)$$

Rate-determining step $\qquad H_3AsO_3 + HIO \quad \overset{\kappa_1}{\rightarrow} \quad H_3AsO_4 + H^+ + I^- \qquad (16)$
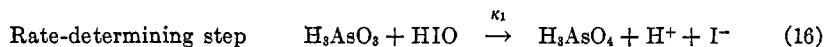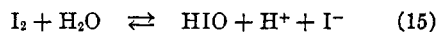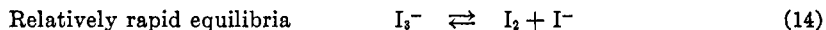
The reverse of 16 is of course the rate-determining step which is responsible for rate-equation 13. The following values of the specific rates are based upon the conventional units—moles per liter and minutes (7)—but are not corrected for salt effects. At $0°$ $k_1 = 9.4 \times 10^{-4}$, $k_2 = 6.3 \times 10^{-3}$ (approximately), $k_1/k_2 = 0.15$, and $K = 0.16$.

The specific rate of the bimolecular reaction between H_3AsO_3 and HIO has been calculated by Liebhafsky (7) from k_1 and the equilibrium constants of reactions 14 and 15 to have the extremely large value: $\kappa_1 = 1 \times 10^{14}$ at $0°$.

Roebuck's results constituted an important item of the evidence which the author presented (8) in 1906 to support the conclusions that (a) when a halogen, X_2, is reduced in aqueous solution the actual reactant frequently is the hypohalous acid, HXO (or the ion XO^-); and (b) when a halide ion, X^-, is oxidized by a substance which loses oxygen in the reaction the primary product is usually the weak acid HXO or the ion XO^-.

In this use of the term "primary product" and, in general, in the formulation of intermediate reactions, there has been no intention of implying that other intermediate compounds do not intervene between the reactants and products listed. The reactants must remain in contact long enough to permit the necessary rearrangements of electrons and atoms to take place, and it is therefore evident that the formation of an addition compound (or compounds) may and probably should be assumed in every case. Even in the case of a first order reaction some interaction with the solvent, water, is in general to be expected.

STEADY STATES IN THE CATALYTIC DECOMPOSITION OF HYDROGEN PEROXIDE

When hydrogen peroxide is added to a solution which contains bromide ion and hydrogen ion at moderately large concentrations, bromine is formed at a measurable rate. Its concentration rises gradually to a definite value in each experiment and then remains constant until the hydrogen peroxide is decomposed. The reaction at the beginning of the experiment is

$$H_2O_2 + 2\,Br^- + 2\,H^+ \xrightarrow{k_1} Br_2 + 2\,H_2O \qquad (17)$$
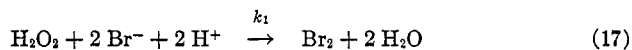
On the other hand bromine is reduced by hydrogen peroxide. The reaction

$$H_2O_2 + Br_2 \xrightarrow{k_2} O_2 + 2\,Br^- + 2\,H^+ \qquad (18)$$
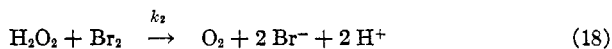
is very rapid when the concentration of either hydrogen ion or bromide ion is low, and proceeds until a concentration of bromine is reached which is too small to be measured experimentally. However, the same final concentration of bromine as in the first

experiment can be realized if the final concentration of the hydrobromic acid and the temperature are the same as in that experiment.   In each case a steady state is reached in which the only measurable reaction is

$$2 H_2O_2 \overset{k}{\rightarrow} O_2 + H_2O \tag{19}$$

The hydrogen peroxide thus is catalytically decomposed in a solution in which the concentration of H^+, Br^- and Br_2 remain constant.

The investigation of this system of reactions was undertaken by Livingston and the author (9) in the hope of proving that this catalysis is nothing more nor less than the occurrence of the independent reactions 17 and 18 at equal rates.   The net result would then be reaction 19, since the bromine terms cancel.   Reactions such as 17 and 18 were termed *compensating reactions* by Abel (18a) and by Bray and Livingston.

A large number of experiments at 25° led to the following results.   The rate of decomposition of hydrogen peroxide at the steady state conforms to the rate law

$$- d(H_2O_2)/dt = k(H_2O_2)(Br^-)(H^+) \tag{20}$$

The concentration of bromine at the steady state is proportional to the square of the product of the concentrations of hydrogen ion and bromide ion, i.e.,

$$(Br_2)/(H^+)^2(Br^-)^2 = R, \text{ a constant.} \tag{21}$$

On the basis of these results and the assumption that reactions 17 and 18 are responsible for the catalysis, it was predicted in the first paper (9a) that the rates of reactions 17 and 18 at a distance from the steady state would follow the laws

$$d(Br_2)/dt = k_1(H_2O_2)(Br^-)(H^+), \text{ where } k_1 = \tfrac{1}{2}k \tag{22}$$

$$- d(Br_2)/dt = k_2(H_2O_2)(Br_2)/(Br^-)(H^+) \tag{23}$$

and that at the steady state, where these rates are equal,
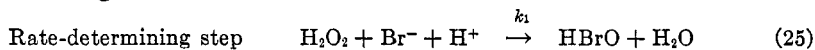
$$k_1/k_2 = R \tag{24}$$

The results of a few experiments (9a) were considered sufficient to prove that rate-equation 22 holds in the initial stages of reaction 17. Final evidence in favor of our assumption was obtained at a later date (9d) from measurements of the rate of reaction 18 at low concentrations of bromide ion—i.e., under conditions where the catalysis is negligible. On account of the high speed of the reaction a flow method was used, which provided for the quenching of the reaction a few seconds after the solutions were mixed. The results at 25° verified equations 23 and 24.

Conclusive evidence of the validity of rate-equation 23 had already been obtained by Balint (10) by direct measurements at 0°, but his thesis, in Hungarian, was overlooked while our work was in progress. His results are summarized in our paper (9d).
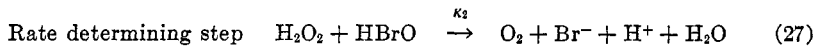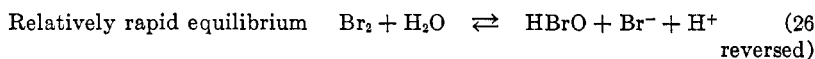
The constants k_1, k_2 and R when corrected for salt effects were designated χ_1, χ_2 and ρ respectively. At 25° $\chi_1 = 0.022$, $\chi_2 = 0.018$, $\chi_1/\chi_2 = 1.2$, and $\rho = 1.2$ to 1.7.

Equations 22, 23 and 24 are formally analogous to equations 2, 4 and 5, or 12, 13 and 5, and furnish similar information about mechanism. Each of the reactions, 17 and 18, has only one rate-determining step, and at the steady state these two rate-determining reactions have the same speed. Here the analogy with a true equilibrium ends, since H_2O_2 is used up in both reactions. However, the bromine compound which is the product in one reaction must be the reactant in the other.

The kinetic mechanism outlined below is in complete agreement with the four sets of experimental data summarized in equations 20, 22, 23 and 24 or 21, and is consistent with the general conclusions about halogen and halide reactions, stated in the preceding section.

Rate-determining step $H_2O_2 + Br^- + H^+ \xrightarrow{k_1} HBrO + H_2O$ (25)

Rapid follow reaction $HBrO + Br^- + H^+ = Br_2 + H_2O$ (26)

The sum is reaction 17.

Relatively rapid equilibrium $Br_2 + H_2O \rightleftarrows HBrO + Br^- + H^+$ (26 reversed)

Rate determining step $H_2O_2 + HBrO \xrightarrow{k_2} O_2 + Br^- + H^+ + H_2O$ (27)

The sum is reaction 18.

The specific rate of the bimolecular reaction between H_2O_2 and HBrO, calculated from k_2 and the equilibrium constant for the bromine hydrolysis is $\kappa_2 = 0.018/5.2 \times 10^{-9} = 3.5 \times 10^6$ at 25°. At the steady state the absolute rates of reactions 25 and 27 are equal. Their sum is reaction 19, and they too are compensating reactions.

The above results evidently would have been more complex if there had been more than one rate-determining step in either of the overall reactions, 17 and 18, or if the mechanism of either of these reactions had undergone a change in the approach to the steady state. Such complications will be illustrated later.

The completeness of the proof of mechanism in the present example supports the chemical theory of homogeneous catalysis, namely, that the catalysis is due to a series of compensating reactions. A catalyst for a homogeneous oxidation-reduction reaction may therefore be expected to exist in at least two forms, which correspond to an oxidation-reduction couple. Thus the qualitative evidence indicated that the bromine–bromide couple catalyzes the decomposition of the peroxide. The steady state function, 21, is not in disagreement with this idea; but the results of the rate measurements, equations 20 and 23, led to the conclusion that the rate-determining reactions involve the hypobromous acid–bromide couple. It is of interest to consider what other couples are eligible to be catalysts for the decomposition of hydrogen peroxide.

The energy relations of hydrogen peroxide reactions in acid solution may be conveniently represented by plotting the electromotive force of half-reactions against the logarithm of the concentration of hydrogen ion. The equations of the half-reactions considered and values of $E°$, the standard oxidation-reduction potential at 25°, are shown at the right-hand side of the diagram; the lines show the effect of varying the concentration of hydrogen ion. The $E°$ values were usually calculated from free-energy or equilibrium data. In this connection it is of interest to note that direct E.M.F. measurements yield values for the O_2–H_2O_2 couple ($E° = 0.68$ volt), but not for the H_2O_2–H_2O or O_2–H_2O couples ($E° = 1.78$ and 1.23, respectively). The dis-

tance between the two hydrogen peroxide lines, 1.10 volts, is a measure of the tendency of hydrogen peroxide to decompose at any concentration of hydrogen ion, H_2O_2 (M concentration) = H_2O (liquid) + $\frac{1}{2}O_2$ (1 atm.).

It is evident that an oxidation-reduction couple, O—R, is eligible to catalyze the decomposition of hydrogen peroxide when its potential lies within the region between the two peroxide lines,
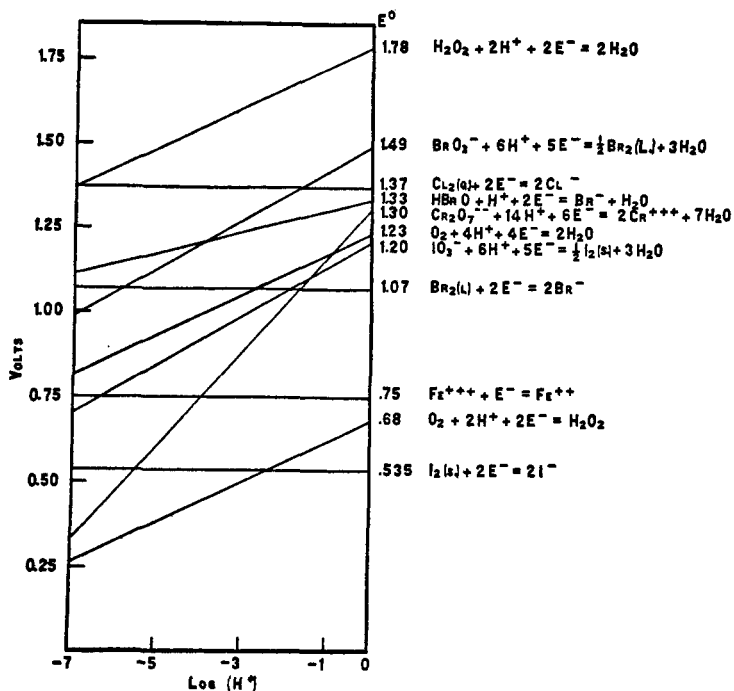

FIG. 1. OXIDATION POTENTIALS AT 25°C.

or may be brought there by a reasonable change in the concentrations of O and R. The tendency of each of the two compensating reactions to take place will then be positive and the sum of these tendencies will equal 1.10 volts. Each of the couples shown in the diagram meets this requirement. However, the free energy data give no evidence concerning the mechanism or speed of the compensating reactions.

In any given case the speed of one or both of these compensating reactions may be so small that the couple will have no appreciable catalytic action, and it is therefore always necessary to determine by experiment whether a couple, selected as a possible catalyst by means of free energy data, actually is a catalyst. The BrO_3^-–Br_2 couple was cited by Bray and Livingston (9a) as an example. BrO_3^- is reduced rather slowly by H_2O_2 in acid solution (9a, 11), but no evidence of the oxidation of Br_2 to BrO_3^-, or of catalysis due to BrO_3^-, has been obtained.

From the value of the oxidation potentials of the Br_2–Br^- and $HBrO$–Br^- couples in the diagram, it may be concluded that each of the reactions, 17, 18, 26 and 27, has a great tendency to take place, and therefore that each of these couples is a possible catalyst; but experiments were necessary to demonstrate the catalysis, and the kinetic investigation to prove that H_2O_2 reacts much more rapidly with $HBrO$ than with Br_2 or Br_3^-.

Ferrous ion is oxidized by H_2O_2 very rapidly and practically completely to Fe^{+++}, and H_2O_2 is catalytically decomposed in a solution which contains Fe^{+++} and H^+. However it is not safe to conclude from the potential of the Fe^{+++}—Fe^{++} couple that the kinetic mechanism is the simultaneous reduction of Fe^{+++} to Fe^{++} and oxidation of Fe^{++} to Fe^{+++}. The rate measurements of von Bertalan (12) and others agree fairly well with the rate law

$$- d(H_2O_2)/dt = k(H_2O_2)(Fe^{+++})/(H^+) \qquad (28)$$

This relation was checked in this laboratory by F. D. Dempster in 1923 for concentrations of H_2O_2 below 0.4 M and above 0.02 M. At lower concentrations the value of k decreased gradually during each run. Recalculation of von Bertalan's data to provide for the decrease in the concentration of acid during the initial oxidation of Fe^{++} to Fe^{+++} brought excellent agreement between the results of these experiments and those in which ferric salt was used. The average value of k is 125 at 40° when concentrations are in moles per liter. With regard to mechanism, it is possible that one of the compensating reactions is the formation of FeO_2H^{++} from $FeOH^{++}$ and H_2O_2 or from Fe^{+++} and HO_2^-, or that FeO_2H^{++} is in equilibrium with Fe^{+++}, H_2O_2 and H^+; but,

even if one of these assumptions is made, nothing definite can be stated about the subsequent history of this unknown intermediate compound. It may reduce H_2O_2 to yield $Fe^{+++} + O_2$, or decompose into $Fe^{+++} + \frac{1}{2} O_2$, or undergo more complex changes. In this connection it should be noted that Bohnson and Robertson (13) have presented optical evidence that ferrate ion is present during the reaction.

An exceptionally large amount of experimental evidence is available in the iodine–iodide system of reactions. H_2O_2 may be determined volumetrically by means of the reaction

$$H_2O_2 + 3\,I^- + 2\,H^+ \xrightarrow{k_1} I_3^- + 2\,H_2O \tag{29}$$
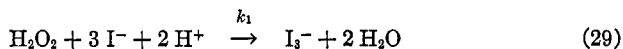
when the concentration of H^+ is 0.2 M (9d) or greater, and catalytic decomposition of H_2O_2 is appreciable only at lower concentrations of acid. The rate measurements of Magnanini (14) in 1891 and of Noyes (15) in 1895–1896 are in agreement with the rate equation

$$d(I_3^-)/dt = k_1(H_2O_2)(I^-) + k_1'(H_2O_2)(I^-)(H^+) \tag{30}$$

and were interpreted (8) to correspond to two simultaneous rate-determining reactions

$$H_2O_2 + I^- \xrightarrow{k_1} IO^- + H_2O \tag{31}$$

$$H_2O_2 + I^- + H^+ \xrightarrow{k_1'} HIO + H_2O \tag{32}$$
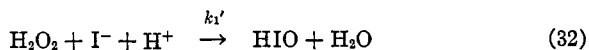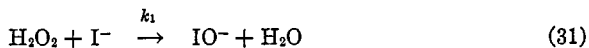
At 25° $k_1 = 0.60$—0.65 and $k_1' = 16$, approximately. The third order reaction is negligible in comparison with the second order reaction when the concentration of H^+ is 10^{-4} or lower, but its specific rate, 16, is much greater than that of the corresponding Br^- reaction, 0.022 in reaction 25.

Brode (16) in 1904, immediately after Walton (17) had demonstrated that the decomposition of hydrogen peroxide in potassium iodide solution obeys the law

$$- d(H_2O_2)/dt = k(H_2O_2)(I^-), \quad k = 1.3 \text{ at } 25°, \tag{33}$$

pointed out that k is equal to $2\,k_1$, and concluded that reaction 31 must be the first step in the catalytic decomposition, as well as in reaction 29.

In 1908 Abel (18) began his extensive investigations of these reactions at concentrations of hydrogen ion between 10^{-7} and 10^{-4}, controlled by the acetic acid–sodium acetate buffer.   He showed that the catalysis is due to a "dynamic equilibrium" or steady state in which the compensating reactions are reaction 29 and
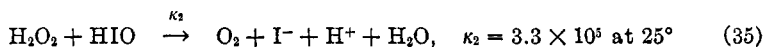
$$H_2O_2 + I_3^- \quad \rightarrow \quad O_2 + 3\,I^- + 2\,H^+ \tag{34}$$
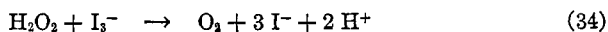
(Abel wrote I_2 instead of I_3^- and defined I_2 as the total iodine.) At any given concentrations of I^- and H^+ the concentration of I_3^- increases or decreases to a definite value, and in this final solution the equilibrium concentrations of I_2, HIO, and IO^- also have definite values.   His rate measurements at and near the steady state proved that the "iodine–iodide" catalysis is the same as the iodide catalysis which Walton had studied in faintly alkaline solutions.   Abel pointed out that it is incorrect to speak of reaction 31 as the only rate-determining step and wrote for the other

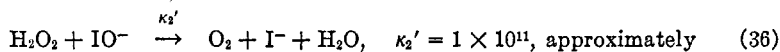$$H_2O_2 + IO^- \quad \rightarrow \quad O_2 + I^- + H_2O$$
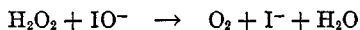
Later (18b) reaction 34 was investigated at a distance from and during the approach to the steady state; the results of a large number of rate-measurements showed the rate law to be very complicated.

Abel in 1928 (18d), from a consideration of the variation of a steady state function, $(H^+)^2(I^-)^2/(I_2)$, with the concentration of hydrogen ion, definitely concluded that oxygen and iodide ion are formed in two rate-determining steps, which together just compensate reaction 31:

$$H_2O_2 + HIO \overset{\kappa_2}{\rightarrow} O_2 + I^- + H^+ + H_2O, \quad \kappa_2 = 3.3 \times 10^5 \text{ at } 25° \tag{35}$$

and

$$H_2O_2 + IO^- \overset{\kappa_2'}{\rightarrow} O_2 + I^- + H_2O, \quad \kappa_2' = 1 \times 10^{11}, \text{ approximately} \tag{36}$$

The values of κ_2 and κ_2' were calculated from rates at the steady state, the concentrations of H^+, I^- and I_3^- at the steady state, and the equilibrium constants for the dissociation of triiodide, the
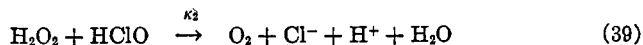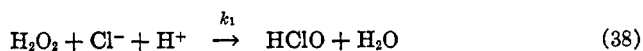
hydrolysis of iodine, and the ionization of hypoiodous acid. He then found that it was possible to interpret the complicated results for reaction 34 by assuming that equilibrium in the hydrolysis of iodine is not maintained at a distance from the steady state.

$$I_2 + H_2O \overset{k_3'}{\underset{k_3}{\rightleftarrows}} HIO + H^+ + I^- \tag{37}$$
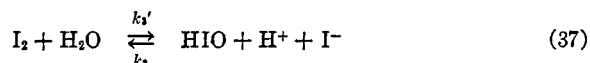
At 25° $k_3' = 0.25$ and $k_3 = K_{\text{equil.}}/k_3' = 0.8 \times 10^{12}$. The value of k_3' was calculated from his rate data for reaction 34.

Recently Liebhafsky (19) has presented experimental evidence that the specific rate of the hydrolysis of iodine at 25° is considerably greater than 0.25. His evidence depends on the high speed of several iodine reactions, e.g., reaction 11 at low concentrations of H^+ and I^-. However, this result, as Liebhafsky was careful to state, casts no doubt upon the correctness of Abel's conclusion that the rate-determining reactions at the steady state are reac-actions 31, 35 and 36.

The catalytic action of the chlorine–chloride couple is similar to but less efficient than that of the bromine–bromide couple. The concentration of chlorine at the steady state is measurable only when the concentration of the hydrochloric acid is 4 N or higher. From measurements of the rate at the steady state and of the function, $(Cl_2)/(H^+)^2(Cl^-)^2$, it was concluded (20) that the two rate-determining reactions are identical in form with reactions 25 and 27:

$$H_2O_2 + Cl^- + H^+ \overset{k_1}{\rightarrow} HClO + H_2O \tag{38}$$

$$H_2O_2 + HClO \overset{\kappa_2}{\rightarrow} O_2 + Cl^- + H^+ + H_2O \tag{39}$$

At 25° in 4.8 M HCl, $k_1 = 10.8 \times 10^{-5}$, and $\kappa_2 = 0.8 \times 10^6$. The limiting or corrected value of k_1 at lower concentrations of HCl was found to be $\chi_1 = 5.0 \times 10^{-5}$, and the corresponding value of κ_2 may be as high as that for the reaction between H_2O_2 and HBrO.

Recent measurements of B. Makower have shown that the rate of the reaction

$$H_2O_2 + Cl_2 \overset{k_2}{\longrightarrow} O_2 + 2\,Cl^- + 2\,H^+ \tag{40}$$
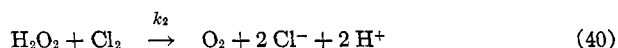
at a distance from the steady state agrees fairly well with the calculated value when the concentration of HCl is in the neighborhood of 5 N. At lower concentrations, however, the measured rate is less than that calculated, and the difference is large at 0.5 M HCl. This discrepancy seems to be due to a remarkable change in the specific rate of the bimolecular reaction between H_2O_2 and HClO, for Makower has found that the rate of this reaction is slow enough to be measured directly when solutions of these substances are mixed at 25° and the concentration of either H^+ or Cl^- is low.

Much experimental material has been collected in this laboratory (21) on the reactions that involve H_2O_2, I_2 and IO_3^-, but the investigation is still incomplete. Hydrogen peroxide is catalytically decomposed in solutions which contain IO_3^- and H^+, and the concentration of iodine is measurable at the steady state. At a low concentration of H^+ solid iodine may separate, and there is also a gradual transition to the iodine–iodide reactions (21b). The steady state in the iodate–iodine catalysis is more complex than that in the halogen–halide catalyses. Thus the steady state concentration of iodine decreases while the hydrogen peroxide is being used up in a run. Also in a narrow range of experimental conditions there was observed (21a, b) a regular periodicity in the rate of evolution of oxygen accompanied by periodic changes in the concentration of iodine.

Liebhafsky (21d) measured the rate of the reaction

$$5\,H_2O_2 + 2\,IO_3^- + 2\,H^+ \longrightarrow 5\,O_2 + I_2 + 6\,H_2O \tag{41}$$
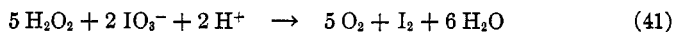
at a distance from the steady state by extracting the iodine as it was formed, and found for the rate law at 50°

$$-\,d(IO_3^-)/dt = 2.6 \times 10^{-4}\,(H_2O_2)(IO_3^-) + 129 \times 10^{-4}\,(H_2O_2)(IO_3^-)(H^+) \tag{42}$$

The two simultaneous rate-determining reactions which are necessary to explain these results were assumed to be:

$$H_2O_2 = IO_3^- \longrightarrow O_2 + IO_2^- + H_2O \tag{43}$$

$$H_2O_2 + IO_3^- + H^+ \longrightarrow O_2 + HIO_2 + H_2O \tag{44}$$
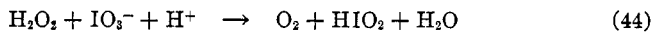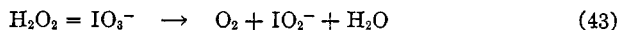
Unpublished rate measurements at the steady state have shown that these two reactions are also rate-determining steps in the catalysis, and that there is at least one additional rate-determining reaction.

The oxidation of iodine in acid solution (21c, e)

$$5\,H_2O_2 + I_2 \;\rightarrow\; 2\,IO_3^- + 2\,H^+ + 4\,H_2O \tag{45}$$
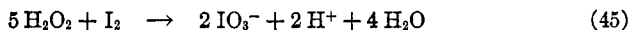
takes place at a measurable rate only when IO_3^- is present, and is always accompanied by catalytic decomposition. The first step has been shown to be the hydrolysis of iodine (equation 37). The reaction proceeds when this equilibrium is shifted by the removal of the products, e.g., by their interaction with IO_3^- and HIO_2. On the basis of our first measurements (21c) it was concluded that the maximum limiting rate had been attained, and that $k_3' = 0.6$ at 25°. Later measurements at 0° (21e) cast doubt upon this result, and, as has already been mentioned, Liebhafsky (19) has recently presented evidence that the specific rate of the iodine hydrolysis has a considerably higher value.

The $Cr_2O_7^{---}$–Cr^{+++} catalysis is also very complicated. The results of Spitalsky (22), however, show that the catalysis takes place under conditions which are intermediate between those for the reduction of $Cr_2O_7^{--}$ to Cr^{+++} and those for the oxidation of trivalent chromium to CrO_4^{--}, and depends upon the rates of these compensating reactions. A steady state is reached at low concentrations of acid, but Spitalsky determined the steady state function only for the limiting case of zero concentration of hydrogen peroxide.

In this review the author has attempted to show that intermediate compounds have been identified in some rather complex reactions in aqueous solution, and that the specific rates of a number of intermediate reactions can be measured. The temperature coefficients, and therefore the heats of activation, of these intermediate reactions either have been, or can be, determined. Such results are of importance in inorganic chemistry, and also may be of value in the search for a theoretical explanation of wide differences in the specific rates of closely analogous reactions.

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