published electron diffraction investigations,[12,13] but later, as yet uncompleted, studies in these Laboratories definitely show that the published conclusions are unsatisfactory.[14] Tetramethylplatinum then provides the first established example of a methyl group bonded to more than one other atom.

Acknowledgment.—The authors are indebted to Professor Henry Gilman for supplying crystals of tetramethylplatinum, and for helpful advice and discussions regarding the chemistry of the platinum alkyls and their derivatives. They benefited also from frequent consultations with Professor Linus Pauling.

Summary

The crystal structures of trimethylplatinum chloride and tetramethylplatinum have been determined. The crystals are isomorphic, with space group T_d^3–$I\bar{4}3m$. The edge of the smallest cubic unit is 10.55 Å. for trimethylplatinum chloride and 10.145 Å. for tetramethylplatinum.

Trimethylplatinum chloride is a tetramer with platinum atoms and chlorine atoms at alternate corners of a distorted cube. Bonded to each platinum are three methyl groups. Tetramethylplatinum is similar, with methyls replacing the chlorines. Two of these tetramers, of point symmetry T_d, compose the body-centered unit.

Interatomic distances involving carbon atoms had to be assumed. The distance Pt–Cl = 2.48 Å., Cl–Cl = 3.28 Å., ∠ Pt–Cl–Pt = 99°. The shortest distance Pt–Pt in $PtMe_3Cl$ is 3.73 Å.; in $PtMe_4$ it is 3.44 Å. The Me–Me distances between adjacent tetramers are slightly more than 4 Å.

Tetramethylplatinum provides the first case where a methyl group is bonded to more than one other atom. Neither compound shows the expected d^2sp bonds to platinum.

PASADENA, CALIFORNIA RECEIVED JANUARY 29, 1947

[13] N. R. Davidson, J. A. C. Hugill, H. A. Skinner, and L. E. Sutton, *Trans. Faraday Soc.*, **36**, 1212 (1940).

[14] Private communication from Professor Verner F. H. Schomaker.

[COMMUNICATION NO. 1137 FROM THE KODAK RESEARCH LABORATORIES]

Oxidation Processes. XVIII.[1] A Classification of Reactions on the Basis of the Semiquinone Theory

BY J. E. LUVALLE AND A. WEISSBERGER

The preceding papers of this series dealt with the oxidation of α-ketols (—CHOHCO—), α-aminoketones (—$CHNH_2CO$), enediols (—COH=COH—), and hydroquinones by oxygen and, in some cases, by cupric salts. Kinetic experiments yielded rate laws which were interpreted in terms of reactive species and reaction mechanisms. For instance, it was shown that in these reactions, the mono- and the divalent anions of the various compounds are more reactive than the neutral molecules and that the monomeric products of univalent oxidation, the semiquinones, occupy key positions in the reactions.[1,2] The present paper derives the observed rate laws in a systematic way, making full use of the equilibria in two-step oxidations and of the concept of the steady state. This treatment gives a classification of the earlier results[1,2,3] and furnishes a ready means for the interpretation of more recent data on aromatic amines.[4]

The existence of semiquinones, *i. e.*, of rather stable free radicals which are intermediate in their state of oxidation between *p*- or *o*-diaminobenzenes and quinonediimines, between hydroquinones and quinones, etc., was first suggested by Hantzsch.[5] They were thoroughly studied and discussed by Weitz.[6] Elema[7] and Michaelis[8] showed independently that bivalent oxidations and reductions proceed in univalent steps and that the intermediate semiquinones are in equilibrium with the reduced and the oxidized forms (dismutation) and with their dimers. Both equilibria are in accord with the radical character of the semiquinones. The values of the respective equilibrium constants are functions of the *p*H,[8,9] because dimerization and dismutation of the ions are inhibited by electrostatic repulsion.[8,10] However, the stability of the semiquinones appears to be primarily caused by resonance.[11] The resonance is smaller if the structures are non-equivalent.

[1] Part XVII, Weissberger and LuValle, THIS JOURNAL, **66**, 700 (1944).

[2] (a) James and Weissberger, *ibid.*, **60**, 98 (1938); (b) Weissberger, LuValle and Thomas, *ibid.*, **65**, 1934 (1943).

[3] (a) James, Snell and Weissberger, *ibid.*, **60**, 2084 (1938); (b) Kornfeld and Weissberger, *ibid.*, **61**, 360 (1939).

[4] LuValle and Weissberger, to be published.

[5] Hantzsch, *Ber.*, **49**, 519 (1916); **54**, 1276 (1921).

[6] Weitz, *Z. Elektrochem.*, **34**, 538 (1928).

[7] Elema, *Rec. trav. chim.*, **50**, 807 (1931); **52**, 569 (1933).

[8] (a) Friedheim and Michaelis, *J. Biol. Chem.*, **91**, 355 (1931); (b) Michaelis, *ibid.*, **92**, 211 (1931); (c) Michaelis, THIS JOURNAL, **53**, 2953 (1931); (d) Michaelis, *Chem. Rev.*, **16**, 243 (1935); (e) Michaelis and Schubert, *ibid.*, **22**, 437 (1938); (f) Michaelis and Smythe, *Ann. Rev. Biochem.*, **7**, 1 (1938); (g) Michaelis, *Ann. N. Y. Acad. Sci.*, **40**, 39 (1940).

[9] Michaelis, Granick and Schubert, THIS JOURNAL, **63**, 351 (1941); Michaelis and Granick, *ibid.*, **63**, 1636 (1941); Schubert, *Ann. N. Y. Acad. Sci.*, **40**, 111 (1940).

[10] Weiss, *Trans. Faraday Soc.*, **42**, 116 (1946).

[11] Pauling, "The Nature of the Chemical Bond," Cornell University Press, Ithaca, 1940, Chap. IV; Wheland, "The Theory of Resonance," John Wiley and Sons, New York, 1944.

In the field of kinetics, several investigators have suggested mechanisms involving semiquinone formation. The present series of papers started with an investigation of the transient blue color in alkaline solutions of benzoin. This color was attributed to the univalent oxidation product of benzoin,[12] which was shown to be in equilibrium with benzoin and benzil.[12,13] Weiss[14] has emphasized the role of semiquinone dismutation in oxidation–reduction mechanisms, and Michaelis[8] suggested that the value of the semiquinone formation constant determines the reversibility of an oxidation–reduction.

The rate of autoxidation of durohydroquinone is governed by the formation of the semiquinone from durohydroquinone and duroquinone.[3a] A similar mechanism prevails in the autoxidation of pseudo-cumohydroquinone[3a] as long as the concentration of the quinone is relatively small. If greater amounts of quinone are added, the effect on the oxidation rate decreases. It was suggested that the autoxidation of hydroquinone, toluhydroquinone and the xylohydroquinones resembles that of pseudo-cumohydroquinone, but that in these cases the concentration of the quinone at which additional amounts of the latter become ineffective is much smaller.[3a] The action of inhibitors was explained on this basis.[3a,15] Semiquinone formation was shown to be important in the autoxidation of ascorbic acid.[3b,16]

The following steps and equilibria of the over-all reaction

$$\mathrm{R} + \mathrm{O_2} \longrightarrow \mathrm{T} + \mathrm{O_2^-}$$

are considered in the present paper. Oxygen may be replaced by other suitable oxidants; but only oxygen will be discussed here.

$$\mathrm{R} + \mathrm{O_2} \xrightarrow{k_1} \mathrm{S} + \mathrm{O_2^-} \tag{1}$$

$$\mathrm{S} + \mathrm{O_2} \xrightarrow{k_2} \mathrm{T} + \mathrm{O_2^-} \tag{2}$$

$$\mathrm{R} + \mathrm{T} \underset{k_{-3}}{\overset{k_3}{\rightleftarrows}} 2\mathrm{S} \tag{3}$$

$$\mathrm{R} + \mathrm{T} \underset{k_{-4}}{\overset{k_4}{\rightleftarrows}} \mathrm{D} \tag{4}$$

$$2\mathrm{S} \underset{k_{-5}}{\overset{k_5}{\rightleftarrows}} \mathrm{D} \tag{5}$$

$$\mathrm{T} + \mathrm{X} \xrightarrow{k_6} \mathrm{Y'} \tag{6}$$

$$\mathrm{T} + \mathrm{S} \underset{k_{-7}}{\overset{k_7}{\rightleftarrows}} \mathrm{T{\cdot}S} \tag{7}$$

$$\mathrm{T{\cdot}S} + \mathrm{S} \longrightarrow 2\mathrm{T} + \mathrm{R} \tag{8}$$

$$2{\cdot}\mathrm{TS} \xrightarrow{k_8} 3\mathrm{T} + \mathrm{R} \tag{8a}$$

R, S and T are the reduced compound, the semiquinone, and the oxidized compound, respectively; D is the dimer; X represents a compound reacting irreversibly with T, *e. g.*, the solvent or hydrogen peroxide, forming Y; and T·S is an addition complex of T and S. All symbols stand for the neutral molecules and the ionic species in instantaneous equilibrium with them, *i. e.*, R in one reaction may be the divalent ion, and the neutral molecule in another reaction. Rate constants are symbolized by k_i, equilibrium constants by K. The first five reactions follow Michaelis's interpretation of his potentiometric data,[8] but we consider the oxidation reactions proper, (1) and (2), irreversible. The equilibria, (3), (4) and (5), represent the formation and dismutation of the semiquinone and the formation of the dimer, by reaction of reduced and oxidized compounds and by dimerization of the semiquinone, respectively. These equilibria are related by the equation

$$K_3 = K_4/K_5 \tag{9}$$

Formation of the complex, T·S, was suggested by Kornfeld and Weissberger[3b] to explain the rate data for ψ-cumohydroquinone.[3a] Equation (8) or (8a) represents the mechanism for the regeneration of T and R demanded by the experimental data. Catalysis and inhibition by foreign substances will be discussed in a subsequent paper.

Reactions (1) and (2) form perhydroxyl ion, $\mathrm{O_2^-}$, in a univalent reduction of oxygen. If we use again one symbol for all ionic species of the same redox state, the fate of $\mathrm{O_2^-}$ may be written as

$$2\mathrm{O_2^-} \underset{k_{-10a}}{\overset{k_{10a}}{\rightleftarrows}} \mathrm{O_2} + \mathrm{O_2^-} \tag{10a}$$

$$\mathrm{R} + \mathrm{O_2^-} \underset{k_{10-b}}{\overset{k_{10b}}{\rightleftarrows}} \mathrm{S} + \mathrm{O_2^-} \tag{10b}$$

$$\mathrm{S} + \mathrm{O_2^-} \underset{k_{-10c}}{\overset{k_{10c}}{\rightleftarrows}} \mathrm{T} + \mathrm{O_2^-} \tag{10c}$$

Reaction (10a) represents the spontaneous dismutation of perhydroxyl.[17] Reactions (10b) and (10c) compete with this dismutation. The balance of the over-all reaction will, in any case, be the same.

If (10a) is much faster than (10b) and (10c), then reaction (10a) regenerates one-half mole of oxygen for each mole of oxygen consumed by reactions (1) and (2). If (10a) is so slow that it can be neglected and $\mathrm{O_2^-}$ is used in reactions (10b) and (10c), then only half the number of oxygen molecules are drawn into the reaction.

Reaction (10b) in combination with (2) would set up a chain mechanism. No signs of such a chain reaction were observed.

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[12] Weissberger, Mainz and Strasser, *Ber.*, **62**, 1942 (1929).

[13] Michaelis and Fetcher, THIS JOURNAL, **59**, 1246 (1937).

[14] Weiss, *Nature*, **133**, 648 (1934); Weiss, *Naturwissenschaften*, **23**, 64 (1935).

[15] (a) James and Weissberger, THIS JOURNAL, **61**, 442 (1939); (b) Snell and Weissberger, *ibid.*, **61**, 450 (1939); (c) Mees, "The Theory of the Photographic Process," The Macmillan Co., New York, N. Y., 1942, p. 381; (d) Weissberger, Thomas and LuValle, THIS JOURNAL, **65**, 1489 (1943).

[16] Dekker and Dickinson, *ibid.*, **62**, 2165 (1940); Silverblatt, Robinson and King, *ibid.*, **65**, 137 (1943).

[17] Latimer, "Oxidation Potentials," Prentice-Hall Co., New York, N. Y., 1938, Chap. IV.

Reaction (10c) immediately following (1) in the same collision represents virtually a one-step bivalent oxidation. However, such a coincidence of (1) and (10c) would scarcely affect the two-step character of the over-all reaction, because (1) is, in general, so slow that it is important only in the absence of T, *i.e.*, in the very beginning of the reaction, and in the presence of inhibitors which remove T or S.[2a,3a]

Reaction (10c), taking place as a separate step in reactions, the rates of which are limited by the formation of S, may double the rate of oxygen absorption but not affect the rate constant of the over-all reaction. In reactions where the formation of S is rapid as compared with (2) and (10c), the reaction of O_2^- according to (10c) increases the rate of oxygen absorption and the rate constant. This increase, is, of course, limited by the formation of O_2^-, according to (1) and (2), and by the dismutation, (10a).

Derivation of Rate Laws

The rate law of a complex reaction may depend upon a step in the sequence of reactions which is slow and therefore rate-determining, and/or on the concentration of a reactive species which is controlled by an equilibrium.

When the rates of the reactions forming and consuming a reactive intermediate in a sequence of reactions are high compared to the difference between the rates, the intermediate is in a "steady state."[18] The concentration of a compound in the steady state may vary in the course of the reaction, *e.g.*, it may be a function of the concentration of an initial reactant, in which case it will decrease as the concentration of the initial reactant decreases. The use of the steady-state concept may be illustrated as follows:

A compound, B, reacts with oxygen at a high rate. Then the oxygen uptake per unit time depends on this rate and on the concentration of B. If B, in turn, is formed in a comparatively slow reaction from A, the rate of the reaction, A → B, determines the oxygen uptake per unit time. For example, α-ketols enolize to form enediols which, in one form or another, react with molecular oxygen.[12] The rate of oxygen consumption was found to be identical with the rate of enolization.[19] Calling the α-ketol A, the enediol B, the oxidation product C, and the rate constants of the reactions k_B and k_C, respectively, we have

$$-\,\mathrm{d}(\mathrm{A})/\mathrm{d}t = \mathrm{d}(\mathrm{B})/\mathrm{d}t$$
$$-\,\mathrm{d}(\mathrm{B})/\mathrm{d}t = \mathrm{d}(\mathrm{C})/\mathrm{d}t$$
$$k_B(\mathrm{A}) - k_C(\mathrm{B})(\mathrm{O_2}) = 0$$

and

$$(\mathrm{B}) = k_B(\mathrm{A})/k_C(\mathrm{O_2}) \qquad (11)$$

i. e., (B) is a function of (A) and (O_2). (O_2) is kept constant during the course of each experimental run, but may differ for different experiments. (B) is not constant, because it varies in proportion to (A), but, inasmuch as (11) is valid, B is in a "steady state."

If B undergoes a simultaneous reaction, B→D, we have

$$-\frac{\mathrm{d}(\mathrm{A})}{\mathrm{d}t} = \frac{\mathrm{d}(\mathrm{B})}{\mathrm{d}t}$$
$$-\frac{\mathrm{d}(\mathrm{B})}{\mathrm{d}t} = \frac{\mathrm{d}(\mathrm{C})}{\mathrm{d}t} + \frac{\mathrm{d}(\mathrm{D})}{\mathrm{d}t}$$
$$k_B(\mathrm{A}) - k_C(\mathrm{B})\,(\mathrm{O_2}) - k_D(\mathrm{B}) = 0$$

and

$$(\mathrm{B}) = \frac{k_B(\mathrm{A})}{k_C(\mathrm{O_2}) + k_D} \qquad (12)$$

Equations of this type are used in the present paper to derive rate laws for the reactions resulting from the interplay of Reactions (1) to (10). No attempt has been made to discuss all possible combinations, but rather to cover those cases for which examples were encountered or are probable and to set a pattern for the treatment of others.

The reactions considered fall into two major classes: In **Class I**, $k_2 > k_3$; in **Class II**, $k_3 > k_2$. The sign > indicates that the difference equals or exceeds a factor of at least 10. Class I appears to comprise those compounds for which the effective semiquinone formation constant,[8] K_s, is smaller than 10^{-2}, while the compounds with greater semiquinone formation constants belong in Class II.

There should exist reactions for which $k_3 \sim k_2$, forming a group between Classes I and II. Moreover, inasmuch as the effective semiquinone formation constant is a function of *p*H, a change in the latter may shift the reaction of a compound from one class to the other. In addition, a change in *p*H may influence reactions which depend on the stability of R or T if the latter changes with *p*H. The *p*H range of measurements is usually limited by the experimental method.

Each major class (I and II) comprises four subclasses as follows:

A. Reactions involving only equations (1), (2) and (3).
B. Reactions complicated by dimer formation (4, 5).
C. Reactions complicated by irreversible destruction of T (6).
D. Reactions complicated by both dimer formation and irreversible destruction of T (4, 5 and 6).
E. Class I may be further complicated by the formation of addition compounds of T and S (7, 8).

The rate of uptake of oxygen is given by

$$-\,\mathrm{d}(\mathrm{O_2})/\mathrm{d}t = {}^1/_2\{k_1(\mathrm{R})(\mathrm{O_2}) + k_2(\mathrm{S})(\mathrm{O_2})\} \qquad (13)$$

The coefficient, 1/2, is necessitated by the action of perhydroxyl according to reactions (10a) and/or (10c). The rate law is derived by substituting in equation (13) the values of (O_2), (R) and (S); S is found by means of a steady-state equation which is solved in terms of R and oxygen. Inas-

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(18) Bodenstein, *Z. Elektrochem.*, **38**, 911 (1932); Christiansen. *Z. physik. Chem.*, **28B**, 303 (1935); Skrabal, *Monatsh.*, **64**, 289 (1934); Hammett, "Physical Organic Chemistry," McGraw-Hill Book Co., New York, N. Y., 1940, pp. 105–109; Hinshelwood, "Kinetics of Chemical Change," Oxford University Press, 1940, p. 149; Kassel, "Kinetics of Homogeneous Gas Reactions," Chemical Catalog Co., New York, 1932, p. 255; Pease, "Equilibrium and Kinetics of Gas Reactions," Princeton University Press, 1942, p. 116.

(19) Weissberger, Dörken and Schwarze, *Ber.*, **64**, 1200 (1931); Weissberger and Dym, *Ann.*, **502**, 74 (1933).

much as (S) depends on (T), the latter must be obtained by the appropriate equations, in several cases by steady-state equations.

Class I-A-1.—Reactions (3) to (8) are negligible; $k_2 > (S) > k_1(R)$. Reaction (1) is rate-limiting; the rate is independent of (T). The steady-state equation for S is

$$k_1(R)(O_2) - k_2(S)(O_2) = 0 \qquad (14)$$

Solving for (S), we get

$$(S) = k_1(R)/k_2 \qquad (15)$$

Substitution of equation (15) into equation (13) gives the rate law

$$-\frac{d(O_2)}{dt} = k_1(R)(O_2) \qquad (16)$$

This is the simplest possible two-step autoxidation. It occurs only if T does not react with R at an appreciable rate. Such autoxidations are probably very slow.

Class I-A-2.—Reactions (4), (5), (6), (7) and (8) are negligible; $k_1(O_2) > k_3(T)$, $k_{-3} > k_3$, $k_{-3}(S) > k_2(O_2)$. Reaction (1) is fast and rate-controlling. The semiquinone dismutates as fast as it is formed. Hence, reaction (2) and the second term of equation (13) are negligible. The rate law is

$$-d(O_2)/dt = {}^1/_2k_1(R)(O_2) \qquad (17)$$

These reactions will also be very slow. Weiss[14] suggested this mechanism for the autoxidation of hydroquinone, assuming that reaction (1) is reversible. It explains the experimental rate data in the absence of foreign substances, but makes it difficult to understand the effect of inhibitors, such as sulfite,[15a] cysteine,[15a] and ascorbic acid.[15d] Baxendale and Lewin[20] use this mechanism in order to explain the rate data for the autoxidation of some leucoindophenols, where the monovalent ion is the reactive species. The available experimental data are also compatible with Class I-E.

Class I-A-3.—Reactions (4), (5), (6), (7) and (8) are negligible; $k_2 > k_3$, $k_2(O_2) > k_{-3}(S)$, $k_3(T) > k_1(O_2)$. Reaction (1) is slow, and significant only in the early stages of the reaction. Reaction (2) consumes S as fast as it is formed by reaction (3), the rate-controlling step. The reaction is autocatalytic. Solution of the steady-state equation for (S) and substitution in equation (13) gives the rate law[20a]:

$$-d(O_2)/dt = k_1(R)(O_2) + k_3(R)(T) \qquad (18)$$

The initial rate depends upon the first term of equation (18) and is first-order with respect to oxygen. Inasmuch as $k_3(T) > k_1(O_2)$, the rate of the remainder of the reaction is independent of the oxygen concentration and proportional to the product (R)(T), *i. e.*, for constant (R), the rate of the quinone-catalyzed reaction varies linearly with T. If we set $k_3 = 1$ and, for convenience, (R) = 20 (in any unit), then we obtain for the course of a reaction the values listed in Table I.

TABLE I

VALUES FOR UPTAKE AND LOG $(a - x)$ FOR CLASS I-A-3

1 % Completion	2 R	3 T	4 Rate $\overline{(R)(T)}$	5 $\frac{100}{(R)(T)}$	6 Time $\sum\frac{100}{(R)(T)}$	7 Log $(a - x)$
0	20	0	0	∞	0	2.000
5	19	1	19	5.26	5.26	1.978
10	18	2	36	2.78	8.04	1.954
15	17	3	51	1.96	10.00	1.930
20	16	4	64	1.56	11.56	1.903
25	15	5	75	1.33	12.89	1.875
30	14	6	84	1.19	14.08	1.845
35	13	7	91	1.10	15.18	1.813
40	12	8	96	1.04	16.22	1.778
45	11	9	99	1.01	17.23	1.740
50	10	10	100	1.00	18.23	1.699
55	9	11	99	1.01	19.24	1.652
60	8	12	96	1.04	20.28	1.602
65	7	13	91	1.10	21.38	1.544
70	6	14	84	1.19	22.57	1.477
75	5	15	75	1.33	23.90	1.398
80	4	16	64	1.56	25.46	1.301
85	3	17	51	1.96	27.42	1.176
90	2	18	36	2.78	30.20	1.000
95	1	19	19	5.26	35.46	0.699
100	0	20	0	∞	∞	

Column 1 lists the extent of the reaction; columns 2 and 3 give the corresponding concentrations of R and T, respectively; and column 4 gives the product (R)(T), *i.e.*, the rate of the reaction depending upon the second term in (14). The value of 1/(R)(T), *i.e.*, of the time necessary for the reaction to advance by the respective increments, is given in column 5. Finite increments instead of differentials are sufficient for our purpose. Column 6 gives the time which has elapsed when the reaction reaches the state of completion listed in column 1, and the corresponding values of log $(a-x)$ are listed in column 7. Figure 1 shows the uptake–time curve constructed from the values in columns 1 and 6 of Table I and the log $(a - x)$-time curve constructed from the values in columns 6 and 7. The uptake curve has a flat inflection at 50% completion. Thereafter, the autocatalysis becomes less pronounced and the log $(a - x)$–curve straightens out correspondingly. The mechanism of Class I-A-3 is that suggested by James and Weissberger[2a] for the autoxidation of durohydroquinone. Their experimental curves resemble closely those of Fig. 1. Another compound which gives similar experimental curves is diaminodurene.[4]

Class I-B.—Reactions (6), (7) and (8) are negligible; $k_2 > k_3$, $k_3(T) > k_1(O_2)$, $k_2(O_2) > k_{-3}(S)$. The reaction will be autocatalytic unless dimer is the end-product, *i.e.*, when $k_4 > k_3 \gg k_{-4}$ and $k_5 > k_3 \gg k_{-5}$. When dimer is the end-product, the rate is slow and is given by the first term of equation (13). Under these conditions (T) and hence

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(20) Baxendale and Lewin, *Trans. Faraday Soc.*, **42**, 126 (1926).

(20a) In all subclasses of Class I, the steady-state concentration of S is assumed to be so small that terms in $(S)^2$ in the steady-state equations are negligible.

(S) reach a steady state. Cysteine appears to belong in this class as the product, cystine, is the dimer.

Class I-C.—Reactions (4), (5), (7) and (8) are negligible; $k_2 > k_3$, $k_3(\mathrm{T}) > k_1(\mathrm{O_2})$, $k_2(\mathrm{O_2}) > k_{-3}(\mathrm{S})$, $10k_3(\mathrm{R}) \gtrsim k_6(\mathrm{X}) \gtrsim k_3(\mathrm{R})$. Dismutation of the semiquinone by reaction (3) is negligible because it is removed by reaction (2) as fast as it is formed. Solving the steady-state equations for (S) and substituting in equation (13) gives the rate law

$$-\frac{\mathrm{d(O_2)}}{\mathrm{d}t} = \frac{k_1k_6(\mathrm{R})(\mathrm{X})(\mathrm{O_2})}{k_6(\mathrm{X}) - k_3(\mathrm{R})} \qquad (19)$$

If X is the solvent or oxygen, $k_6(\mathrm{X})$ may be written k_6', because X is present in large excess. The steady-state rate is given by equation (19); the extent of the autocatalytic period depends upon the nature of X and $k_6(\mathrm{X})/k_3(\mathrm{R})$.

This class is limited to values of k_6 in the range defined. If $k_6(\mathrm{X}) < k_3(\mathrm{R})$, the reaction will be autocatalytic throughout. If $k_6(\mathrm{X}) \gg k_3(\mathrm{R})$, autocatalysis becomes negligible because of the removal of T by reaction (6), and the rate law becomes identical with that for Class I-A-1.

It was mentioned earlier that the kinetic data on the autoxidation of diaminodurene agree with the rate law of Class I-A-3. Actually, diaminodurene belongs in Class I-C, because the product isolated is duroquinone rather than duroquinonediimine.[4] Inasmuch as duroquinone acts as a catalyst, it becomes equivalent to duroquinonediimine, and the reaction proceeds according to Class I-A-3.

Class I-D.—Reactions (7) and (8) are negligible; $k_2 > k_3$, $k_3(\mathrm{T}) > k_1(\mathrm{O_2})$, $k_2(\mathrm{O_2}) > k_{-3}(\mathrm{S})$, $k_3 > k_{-3}$, $10k_3 \gtrsim k_4 \gtrsim k_3$, $k_4 \gtrsim k_{-4}$, $10k_3(\mathrm{R}) \gtrsim k_6(\mathrm{X}) \gtrsim k_3(\mathrm{R})$. The initial rate is given by the first term of equation (13). Solution of the steady-state equation for (S) and substitution into Equation (13) gives a rate law for the autocatalytic period which is identical with that of equation (18). Solution of the steady-state equations for (T) and (S) and substitution into equation (13) gives the steady-state rate law

$$-\frac{\mathrm{d(O_2)}}{\mathrm{d}t} = \frac{\{k_4(\mathrm{R}) + k_6(\mathrm{X})\}\, k_1(\mathrm{O_2}) + k_3k_{-4}(\mathrm{D})}{(k_4 - k_3) + k_6\dfrac{(\mathrm{X})}{(\mathrm{R})}} \qquad (20)$$

If X is the solvent, $k_6(\mathrm{X})$ may be written as k_6' and the steady state is established near the beginning of the reaction. If X is hydrogen peroxide, its initial concentration is zero and the autocatalytic period may extend over a considerable portion of the reaction.

For the early stages of the autoxidation of catechol in the *p*H range from 6.5 to 10, Joslyn and Branch[21] found a rate law

$$\text{Rate} = K_2\frac{(\mathrm{C})^2}{C + A} \qquad (21)$$

where C is the total concentration of catechol, A is a constant equal to 0.02, and K_2 is a function of

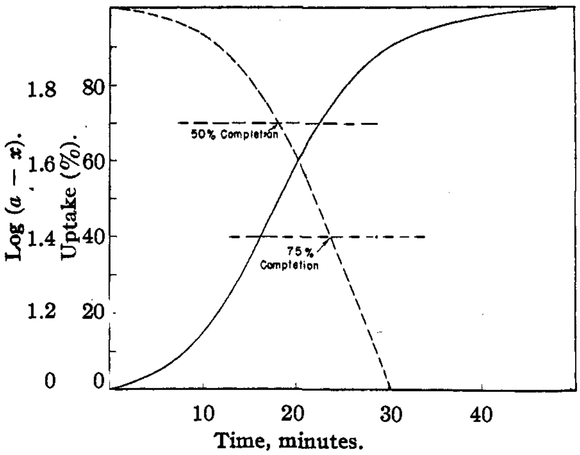

Fig. 1.—Class I-A-1: ——— oxygen uptake; — — — — log $(a - x)$.

*p*H. The rate is first-order with respect to the reciprocal of the hydrogen-ion concentration. When the *p*H variation is included in the rate law, the latter becomes

$$V\alpha(\mathrm{Cat}^-)(\mathrm{O_2})X\,\frac{C}{C + A} \qquad (22)$$

where (Cat^-) is the concentration of the univalent catechol ion and V is the velocity of absorption of oxygen. Above *p*H 10.0 and below *p*H 6.5, the experimental rates are high, and the difference is attributed to the oxidation of the divalent catechol ion and of the neutral molecule, respectively.

o-Benzoquinone is much less stable than the *p*-quinone[22]; therefore, reaction (6) will be much more important.

If we recall that R is used as the symbol for any ionic species and assume that in the case of catechol reactions (3) and (4) involve the neutral molecule, while reaction (1) involves the monovalent ion, equation (20) becomes

$$-\frac{\mathrm{d(O_2)}}{\mathrm{d}t} = \frac{k_1(\mathrm{R^-})(\mathrm{O_2})\{k_4(\mathrm{R}) + k_6(\mathrm{X})\} + k_3k_{-4}(\mathrm{D})(\mathrm{R})}{(k_4 - k_3)(\mathrm{R}) + k_6(\mathrm{X})} \qquad (20a)$$

Assume that k_6 or $k_6(\mathrm{X}) = A = 0.02$, *i. e.*, the quinone decomposes spontaneously or reacts with the solvent. Also assume that $(k_4 - k_3) \sim 1$, which is consistent with the limitation, $10k_3 \gtrsim k_4 \gtrsim k_3$. The rate law becomes

$$-\frac{\mathrm{d(O_2)}}{\mathrm{d}t} = k_1k_4(\mathrm{R^-})\,\frac{(\mathrm{R})\,(\mathrm{O_2})}{(\mathrm{R}) + 0.021} + k_1(\mathrm{R^-})(\mathrm{O_2})\,\frac{0.02}{(\mathrm{R}) + 0.02} + \frac{k_3k_{-4}(\mathrm{D})(\mathrm{R})}{\mathrm{R} + 0.02} \qquad (20b)$$

The first term of equation (20b) is greater than the second term by the factor, $k_4(\mathrm{R})/0.02$. As $k_4 \gg 0.02$, the contribution of the second term to the rate is very small. The third term makes a small contribution to the rate when $k_1k_4\,(\mathrm{R^-})(\mathrm{O_2}) > k_3k_{-4}(\mathrm{D})$, *i. e.*, when (D) and/or k_{-4} are

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[21] Joslyn and Branch, THIS JOURNAL, **57**, 1779 (1935).

[22] (a) Conant and Fieser, *ibid.*, **46**, 1858 (1924); (b) Fieser, *ibid.*, **52**, 5204 (1930).

small. Under these conditions, the rate law is given by the first term of equation (20b), which is identical with equation (22) where k_1k_4 is the proportionality constant.

Class I-E.—Reaction (5) is negligible; $k_2 > k_3$, $k_3(\mathrm{T}) > k_2(\mathrm{O_2})$, $k_2(\mathrm{O_2}) > k_{-2}(\mathrm{S})$, $k_3 > k_{-3}$, $k_4 > k_{-4} > k_8$, $k_7 \gg k_{-7}$, $k_8(\mathrm{S}) > k_{-7}$. The equilibrium (4) is established so rapidly that $k_{-4}(\mathrm{D}) = k_4(\mathrm{R})(\mathrm{T})$, hence a shift in this equilibrium does not affect the rate of oxygen absorption. Reaction (6) is negligible during the beginning of the reaction but may become important in the latter part of the reaction. Reaction (8) is very fast. The effect of a variation of k_7 is discussed below. When reaction (6) is negligible, T does not reach a steady state. Solution of the steady-state equation for (S) and (T·S) gives

$$(\mathrm{S}) = \frac{k_1(\mathrm{R})(\mathrm{O_2}) + 2k_3(\mathrm{R})(\mathrm{T})}{k_2(\mathrm{O_2}) + 2k_7(\mathrm{T})} \tag{23}$$

When $2k_7(\mathrm{T}) < k_2(\mathrm{O_2})$, terms in $k_7(\mathrm{T})$ in the denominator of equation (23) are dropped, and substitution into equation (13) gives the rate law of equation (18). The first term of equation (18) gives the initial rate and the second term, the autocatalytic rate.

When $2k_7(\mathrm{T}) \sim k_2(\mathrm{O_2})$, substitution of equation (23) into equation (13) gives the rate law for the steady state

$$-\frac{\mathrm{d}(\mathrm{O_2})}{\mathrm{d}t} = \frac{\{k_1k_2(\mathrm{O_2}) + [k_1k_7 + k_2k_3](\mathrm{T})\}(\mathrm{R})(\mathrm{O_2})}{k_2(\mathrm{O_2}) + 2k_7(\mathrm{T})} \tag{24a}$$

Kornfeld and Weissberger used a simplified version of equation (24a) and showed that the rate dependency with respect to oxygen is somewhat less than first-order.[8b] As (T) is zero at the start, the reaction is initially autocatalytic, according to equation (18). This period is followed by a transition to the steady-state rate of equation (24a). The autocatalytic period becomes shorter as k_7 increases.

When $2k_7(\mathrm{T}) > k_2(\mathrm{O_2})$, terms in $k_2(\mathrm{O_2})$ in the denominator of equation (23) may be dropped and substitution into equation (13) gives the rate law for the steady state

$$-\frac{\mathrm{d}(\mathrm{O_2})}{\mathrm{d}t} = \frac{k_1k_7 + k_2k_3}{2k_7}(\mathrm{R})(\mathrm{O_2}) + \frac{k_2k_1}{2k_7}\frac{(\mathrm{R})(\mathrm{O_2})^2}{(\mathrm{T})} \tag{24b}$$

The second term of equation (24b) contributes only little and the rate is therefore first-order with respect to oxygen.

The autocatalytic period decreases as $k_7(\mathrm{T})/k_2(\mathrm{O_2})$ increases. Steric hindrance which prevents the formation of the dimer will also prevent the formation of the addition complex, T·S. k_7 can therefore be expected to increase as k_4 increases, *i. e.*, the length of the autocatalytic period should increase with methylation.

Length of the autocatalytic period refers to the percentage of the reaction completed prior to the establishment of the steady state.

According to equations (23), (24a) and (24b), the length of the autocatalytic period is proportional to the concentration of S at which the latter reaches the steady state. Inasmuch as, according to the preceding, this critical concentration of S increases with the oxygen pressure, the length of the autocatalytic period increases with the oxygen pressure.

Reaction (7) does not become significant until $2k_7(\mathrm{T}) \sim k_2(\mathrm{O_2})$ and $k_3(\mathrm{R}) \sim k_7(\mathrm{S})$. This implies that the steady state is not established either until (T) reaches a certain value independent of the initial concentration of R, or until (T)/(R) reaches a certain value independent of the initial concentrations of R and T. When the steady state is established close to the start of the reaction, the two cases cannot be separated. However, if the steady state is established late in the reaction, the two cases can be distinguished experimentally. We consider the case in which the steady state is established at 50% completion and calculate the rate at the establishment of the steady state for values of $(\mathrm{R_0})$ ranging from a to 20a according to (24a) and (24b), respectively. The steady-state rate increases faster than $(\mathrm{R_0})$ if (T) determines the length of the autocatalytic period. If, on the other hand, (T)/(R) determines the length of the autocatalytic period, the steady-state rate is proportional to $(\mathrm{R_0})$. The departure from first-order when equation (24a) gives the rate law depends upon the ratio

$$\frac{\{k_1k_2(\mathrm{O_2}) + [k_1k_7 + k_2k_3](\mathrm{T})\}}{k_2(\mathrm{O_2}) + 2k_7(\mathrm{T})}$$

The departure will be greatest when k_1 is completely negligible; it becomes smaller as $k_7(\mathrm{T})$ assumes values much larger than $k_2(\mathrm{O_2})$.

Variation of the initial values of (T) and (R) will quickly distinguish between the two cases. If (T) is zero at the start, and the initial concentration of R is varied, the length of the autocatalytic period will be independent of (R) if the value of (T)/(R) determines the end of the autocatalytic period. The length of the autocatalytic period will vary inversely with (R) if the value of (T) determines the end of the autocatalytic period. If the initial concentration of R is held constant and the initial concentration of T is varied, the autocatalytic period will end when (T)/(R) reaches a certain value in all cases or it will end when (T) exceeds a certain value in all cases.

If reaction (8a) represents the removal of T·S, then all terms in k_7 in equations (23), (24a), (24b) and (25) are multiplied by one half.

When reaction (6) is not negligible and (T) reaches a steady state, solution of the steady-state equation and substitution into equation (13) gives the rate law

$$-\frac{\mathrm{d}(\mathrm{O_2})}{\mathrm{d}t} = {}^1/_2k_1(\mathrm{R})(\mathrm{O_2}) + \frac{k_1k_2(\mathrm{R})(\mathrm{O_2})\{k_6(\mathrm{X}) + k_3(\mathrm{R})\}}{2k_1k_7(\mathrm{R}) + 2k_2\{k_6(\mathrm{X}) - k_3(\mathrm{R})\}} \tag{25}$$

If the products of reaction (6) undergo autoxidation, the uptake of oxygen is increased and equation (25) does not give the complete rate law.

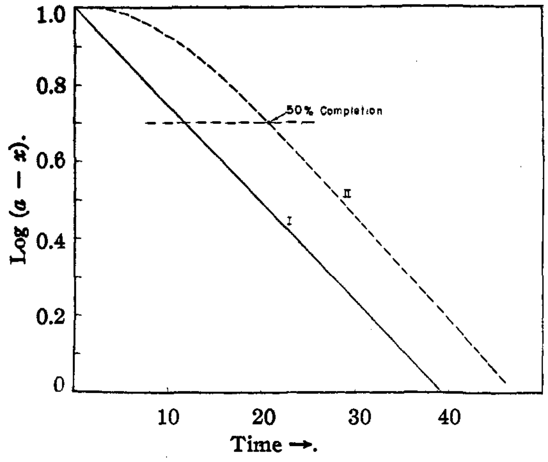

Fig. 2.—Class I-B-1: ——— steady state of S established at the start of the reaction; — — — steady state of S established at 50% completion of the reaction.

Figure 2 gives the log $(a - x)$ *vs.* time curves for reactions in which the steady state is reached virtually immediately and at 50% completion, respectively. Reaction (6) has been neglected. If this reaction is significant, the log $(a - x)$ *vs.* time curves approach the abcissas asymptotically.

Pseudo-cumohydroquinone autoxidizes below *p*H 8.5 by the mechanism of equations (18) and (24a) but above *p*H 8.5 equation (24a) is replaced in the latter part of the reaction by equation (25).[3a,23] Xylohydroquinone, toluhydroquinone and hydroquinone autoxidize at all values of *p*H investigated, by the mechanism of equations (18) and (24b) and in the latter portions of the reaction by equation (25).[3a,24] Durohydroquinone represents the limiting case of this mechanism in which reactions (4), (5), (6) and (7) are negligible.[2a]

The autoxidation of *l*-ascorbic acid below *p*H 7.0 is primarily that of the monovalent ion and the autoxidation above *p*H 7.0 is primarily that of the divalent ion.[2b] Below *p*H 7.0, the rate is independent of the oxygen pressure and some indications of autocatalysis were observed. Dehydroascorbic acid, T, is fairly stable in acid solution, and the kinetic results agree with the reaction mechanism, I-A-3 or I-E. With higher *p*H, dehydroascorbic acid becomes very unstable, and the autoxidation of the divalent ion above *p*H 7.0 gives no indication of autocatalysis.

Class II-A-I.—Reactions (4), (5), (6), (7) and (8) are negligible; $k_2 > k_1$, $k_1(R) > k_2(S)$, $k_2(O_2) > k_{-3}(S)$. The result will be a two-step reaction in which semiquinone accumulates until virtually all of the primary reactant has disappeared. Then, the semiquinone is oxidized to T. The rate of the first step is given by equation (13), the term involving the semiquinone being small. The rate of the second step is given by the second term of equation (13). The autoxidation of Wurster's Blue near *p*H 8.0 appears to have this mechanism.[4]

Class II-A-2.—Reactions (4), (5), (6), (7) and (8) are negligible; $k_1 > k_3$, $k_{-3}(S) > k_2(O_2)$, $k_{-3} > k_3$. Dismutation of the semiquinone, (3), dominates semiquinone formation, (3), and autoxidation of the semiquinone, (2). The rate law becomes identical with that of Class I-A-2.

Class II-A-3.—Reactions (4), (5), (6), (7) and (8) are negligible; $k_3 \gtrsim k_{-3}$, $k_{-3}(S) > k_2(O_2)$, $k_2(S) > k_1(R)$. Reaction (1) is very slow and of importance only in the initial phase of the reaction. After that, the equilibrium, (3), controls the rate of autoxidation. The concentration of semiquinone throughout the reaction is given by the expression of Michaelis[8]

$$(S) = \frac{\sqrt{1 + \gamma(1 - \mu^2)} - 1}{\gamma}(R_0) \qquad (26)$$

where $\mu = (2a - R_0)/R_0$, a is moles oxygen absorbed per mole of R_0, (R_0) is the initial concentration of R, and $\gamma = (4 - K_3)/K_3$. In Fig. 3, values of $(S)/(R_0)$ are plotted against moles of oxygen absorbed. The ratio, $(S)/(R_0)$, and therefore the semiquinone concentration go through a maximum at 50% oxidation. Substitution of (26) in (13) gives the rate law

$$-\frac{d(O_2)}{dt} = 1/2\, k_1(R)(O_2) + \frac{\sqrt{1 + \gamma(1 - \mu^2)} - 1}{2\gamma} k_2(R_1)(O_2) \qquad (27)$$

The first term is negligible except at the start of the reaction. Comparison of (26) and (27) shows that the rate also goes through a maximum at 50% completion.

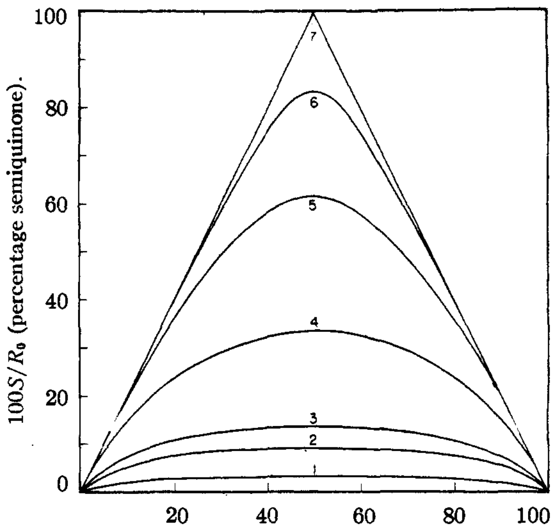

Fig. 3.—Percentage semiquinone for different values of K_3: (1) $K_3 = 10^{-3}$; (2) $K_3 = 10^{-2}$; (3) $K_3 = 10^{-1}$; (4) $K_3 = 1$; (5) $K_3 = 10$; (6) $K_3 = 10^2$; (7) $K_3 > 10^3$.

For the construction of uptake and log $(a - x)$–time curves, we choose $K_3 = 1$, 10 and 100, respectively, and set for convenience $R_0 = 10$ (in any units). Columns 1 and 2 in Table II give the

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(23) LuValle and Weissberger, THIS JOURNAL, 69, 1576 (1947).

TABLE II

VALUES FOR UPTAKE AND LOG $(a - x)$ FOR CLASS II-A-3

1	2	3	4	5	6	7	8	9	10	11
		$K_3 = 1$			$K_3 = 10$			$K_3 = 100$		
% Completion	Log $(a - x)$	Rate S/R_0	R_0/S	Time $\Sigma R_0/S$	Rate S/R_0	R_0/S	Time $\Sigma R_0/S$	Rate S/R_0	R_0/S	Time $\Sigma R_0/S$
0	1.000	0.000	∞	0	0.000	∞	0	0.000	∞	0
5	0.978	.084	11.9	11.9	.097	10.3	10.3	.097	10.4	10.4
10	.954	.146	6.85	18.8	.192	5.22	15.5	.200	5.00	15.4
15	.930	.197	5.08	23.8	.278	3.60	19.1	.297	3.36	18.8
20	.903	.238	4.20	28.0	.359	2.78	21.9	.399	2.52	21.3
25	.875	.267	3.74	31.8	.430	2.32	24.2	.491	2.04	23.3
30	.845	.290	3.35	35.1	.492	2.08	26.3	.576	1.74	25.1
35	.813	.310	3.22	38.3	.542	1.85	28.1	.667	1.50	26.6
40	.778	.323	3.10	41.4	.577	1.73	29.9	.748	1.34	27.9
45	.740	.332	3.08	44.5	.605	1.65	31.5	.810	1.23	29.1
50	.699	.340	2.94	47.5	.615	1.63	33.2	.834	1.20	30.3
55	.652	.332	3.08	50.5	.605	1.65	34.8	.810	1.23	31.6
60	.602	.323	3.10	53.6	.577	1.73	36.5	.748	1.34	32.9
65	.544	.310	3.22	56.9	.542	1.85	38.4	.667	1.50	34.4
70	.477	.290	3.35	60.2	.492	2.08	40.5	.576	1.74	36.1
75	.398	.267	3.74	64.0	.430	2.32	42.8	.491	2.04	38.2
80	.301	.238	4.20	68.2	.359	2.78	45.6	.399	2.52	40.7
85	.176	.197	5.08	73.2	.278	3.60	49.2	.297	3.36	44.1
90	.000	.146	6.85	80.1	.192	5.22	54.4	.200	5.00	49.1
95	− .301	.087	11.9	92.0	.097	10.3	64.7	.097	10.4	59.5
100	...	0	∞	∞	.000	∞	∞	.000	∞	∞

extent of the reaction and the corresponding values of log $(a - x)$. Columns 3, 6 and 9 give the values of the rate, S/R_0, for K_3 equal to 1, 10 and 100. Columns 4, 7 and 10 give the corresponding values of the time interval, (R_0/S), *i. e.*, the time necessary for the reaction to advance by the respective increments, and columns 5, 8 and 11 give the corresponding values of $\Sigma R_0/S$, *i. e.*, the time which has elapsed when the reaction reaches the state of completion indicated in column 1.

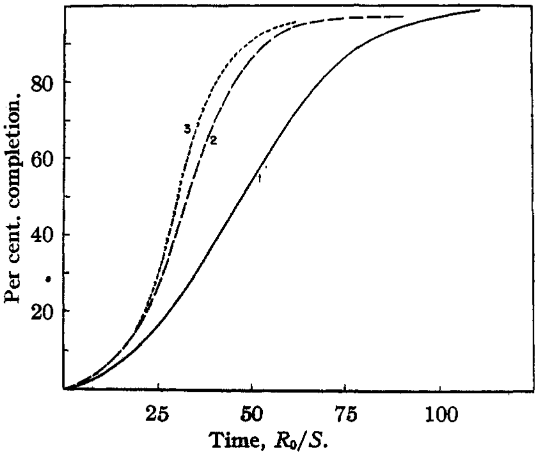

Fig. 4.—Class II-A-1: oxygen uptake: ———, $K_3 = 1$; — — — $K_3 = 10$; - - - - - $K_3 = 10^2$.

Figure 4 contains the plot of uptake *vs.* time and Fig. 5 the corresponding log $(a - x)$–time curves. The uptake–time curves are sigmoid, while the log $(a - x)$–time curves decrease in slope and approach asymptotically a minimum slope. As K_3 increases, the minimum slope is reached earlier in the reaction. For $K_3 > 1000$, the slope becomes constant at 50% completion, because all of R is present as semiquinone (*cf.* Fig. 6). The minimum slope, thereafter, gives the specific rate constant for the autoxidation of the semiquinone.

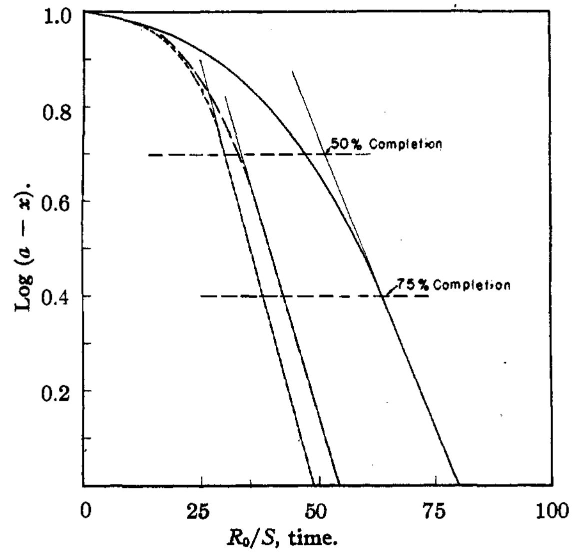

Fig. 5.—Class II-A-1: log $(a - x)$: ———, $K_3 = 1$; — — — $K_3 = 10$; - - - - - $K_3 = 10^2$.

For $K_3 < 10^3$, the specific rate constant of the semiquinone is given by the asymptotic limiting slope of the log $(a - x)$–time curve. Experimentally, a constant limiting slope is frequently reached well before the end of the reaction. This takes place because near the end of the reaction virtually all of R has been converted to semiquinone. Figure 6 shows the variation in R with the extent of the reaction for several values of K_3.

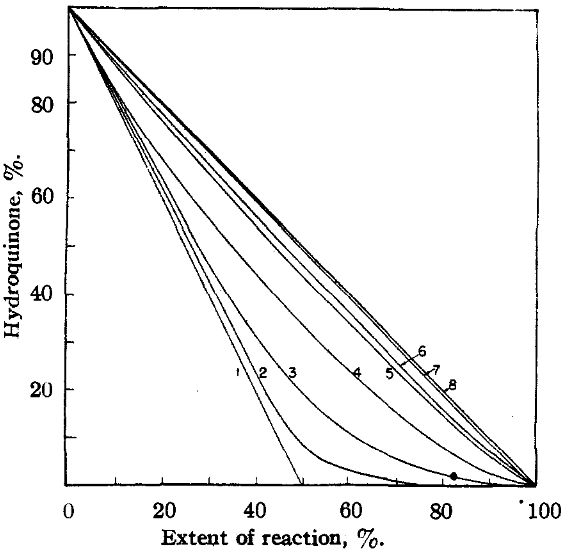

Fig. 6.—Percentage hydroquinone against extent of reaction for different values of K_3: (1) $K_3 = 10^3$; (2) $K_3 = 10^2$; (3) $K_3 = 10$; (4) $K_3 = 1$; (5) $K_3 = 10^{-1}$; (6) $K_3 = 10^{-2}$; (7) $K_3 = 10^{-3}$; (8) $K_3 < 10^{-6}$.

Class II-B.—Reactions (6), (7) and (8) are negligible; $k_3 \gtrsim k_{-3}$, $k_4 \gtrsim k_{-4}$, $k_3 \sim k_4$, $k_{-3} \sim k_5$, $k_5 \gtrsim k_{-5}$, $k_3 > k_2$, $k_2(\mathrm{S}) > k_1(\mathrm{R})$. The simultaneous presence of dimer and semiquinone in measurable quantities makes the solution of equations feasible only for given numerical values of the rate constants. If $k_4 > k_3 \gg k_{-4}$ and $k_5 > k_3 \gg k_{-5}$, that is, dimer is the end-product, the rate becomes that of Class I-B where dimer is the end-product.

Class II-C.—Reactions (4), (5), (7) and (8) are negligible; $k_3 \gtrsim k_{-3}$, $k_{-3}(\mathrm{S}) > k_2(\mathrm{O_2})$, $k_2(\mathrm{S}) > k_1(\mathrm{R})$. If $k_6(\mathrm{X}) > k_3(\mathrm{R})$, the rate becomes identical with that of Class I-C. If $k_6 \sim k_3$ and X is the solvent, $(\mathrm{X}) \gg (\mathrm{R})$; hence, the rate is that of Class I-C; If X is hydrogen peroxide, reaction (6) will not become important until after the first third of the reaction is completed. If the product of reaction (6) is autoxidizable, the log $(a - x)$ *vs.* time curve will become sigmoid in shape as in Fig. 7. The extent of the sigmoid alteration depends upon the relative values of $k_6(\mathrm{X})$ and $k_3(\mathrm{R})$ and the autoxidizability of the product of reaction (6).

Class II-D.—Reactions (7) and (8) are negligible. Other conditions are same as Class II-B. If $k_6(\mathrm{X}) > k_3(\mathrm{R})$, the rate of removal of T may create the conditions of Class I-D. If $k_6(\mathrm{X}) \sim k_3(\mathrm{R})$, the solution of the equations becomes feasible only for given values of the rate constants.

All of the *p*-phenylenediamines appear to react according to Classes II-A-1, II-A-3, II-C and perhaps II-D. In the two latter cases, the value of k_6 is so small that it causes a distortion of the log $(a - x)$ curve only in the latter portion of the reaction when the hydrogen peroxide concentration becomes much greater than (R).[4]

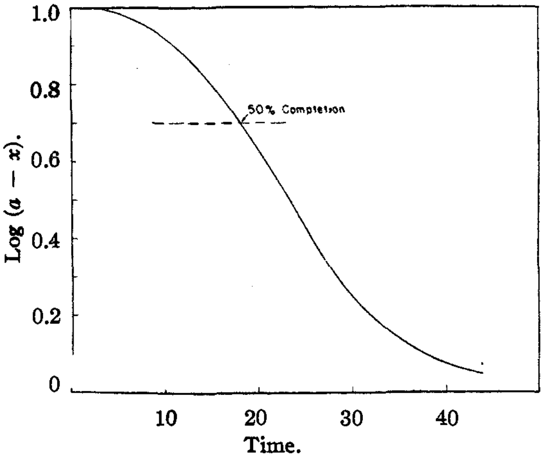

Fig. 7.—Class II-C-2: log $(a - x)$-time curve.

The foregoing derivations may now be summarized. In the mechanisms of Class I, the rate of formation of semiquinone is always the rate-limiting factor. The reactions are autocatalytic unless dismutation, dimer formation, or irreversible destruction of·T create a steady state. Colored intermediates do not appear in these reactions as long as abundant oxygen is present, because they are consumed as fast as they are formed. A compound which at high oxygen concentration reacts according to Class I may at low oxygen concentration react according to Class II.

In the mechanisms of Class II, the rate of autoxidation of the semiquinone is the rate-limiting factor. However, when lack of T due to dimer formation or irreversible destruction lowers the rate of semiquinone formation below the rate of semiquinone oxidation, the mechanism becomes that of the corresponding Class I. Colored intermediates characterize Class II.

If the rate is determined by a relatively slow formation of an autoxidizing tautomer, the latter may then react according to any of the classes. Colored intermediates are likely to appear when the autoxidation mechanism is that of Class II.[12]

Acknowledgment.—We wish to thank Dr. G. Kornfeld and Mr. D. S. Thomas, of these Laboratories, for discussions which helped to clarify some of the concepts presented in this paper.

Summary

Rate laws have been derived for the oxidation of compounds which form semiquinones as intermediates.

A classification of these rate laws has been obtained according to the reactions and equilibria involved.

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