empirical equations for diffusion current. In each case the experimental diffusion current was much lower than the calculated value.

Discussion.—The chemical nature of the material undergoing reduction at the dropping electrode is not clear. The double wave could result from the presence of two reducible species, but probably represents the stepwise reduction of a single species. The similarity of waves obtained in the hydrazine and in the phenylhydrazine solution (where the azine cannot form) suggests but does not prove that the hydrazone is the major product. In any case, mathematical analysis of the first carbonyl-hydrazine wave shows that the electroreduction is irreversible, a value of 0.62 electron transferred being found.

The relatively low diffusion currents obtained at high concentrations and with carbonyl mixtures suggest that equilibrium exists in the system. At very low carbonyl concentrations the hydrazine–carbonyl concentration ratio will approach infinity and the equilibrium, if it exists, will be displaced toward complete reaction. Under these conditions the term in C^2 will become negligible and the current will be determined principally by A and C. Thus the constant A is related to the diffusion coefficient and the irreversibility factors, while B is related to the equilibrium constant of the reaction or reactions.

The mean deviation of all values for R is about 4% and is about three times the mean deviation of values for the chloride diffusion current. The increased deviation is due to the carbonyl wave, possibly because the system has not been adequately controlled. It is more probable, however, that the increased deviation is due to difficulties in locating precisely the inflection point between the carbonyl waves and to the possibility that the recorded wave, resulting from a dynamic instrument, does not accurately or consistently represent the rapidly changing electrode processes in the region of an inflection point.

Summary

It has been shown that aldehydes and ketones can be analyzed polarographically in acid hydrazine solution. The relationship between diffusion current and concentration has been determined for one aldehyde and three ketones over the range 0.0001 M to 0.01 M, and has been expressed by second degree equations. The precision of the method varies between 2 and 5%.

NEWARK, DELAWARE RECEIVED JANUARY 3, 1944

[COMMUNICATION NO. 963 FROM THE KODAK RESEARCH LABORATORIES]

Oxidation Processes. XVII.[1] The Autoxidation of Ascorbic Acid in the Presence of Copper

BY A. WEISSBERGER AND J. E. LUVALLE

Introduction

In the preceding paper of this series we reported on the autoxidation of *l*-ascorbic acid at *p*H from 4.7 to 9.2, in the presence of sufficient cyanide and thiocyanate to suppress the catalytic action of metals. Under these conditions, both the monovalent and the divalent ion of the acid participate in the reaction. With oxygen of atmospheric pressure, the divalent ion reacts 10^5 times faster than the monovalent ion. If the partial pressure of the oxygen is reduced to 1/5, the reaction rate of the divalent ion sinks in proportion to the oxygen concentration, but not the reaction rate of the monovalent ion. The latter ion undergoes a slow process before it reacts with the oxygen, probably forming a reactive radical in the interaction with dehydroascorbic acid. In the absence of cyanide and thiocyanate and in the presence of copper, the reaction rate of the monovalent ion is proportional to the oxygen concentration.[1] This shows that the metal-catalyzed autoxidation of the monovalent ion is more rapid than the slow process just mentioned. The question arises whether the effect of the metal on the reaction of the monovalent ion explains fully the metal catalysis in the autoxidation of ascorbic acid, or whether the autoxidations of unionized ascorbic acid and divalent ion are likewise catalyzed by copper. This problem is treated in the present paper.

(1) Part XVI, Weissberger, LuValle and Thomas, THIS JOURNAL, **65**, 1934 (1943). (On p. 1936, right column, line 15, it should read 0.001 *m* mole instead of 0.001 mole.)

Materials and Methods

***l*-Ascorbic Acid.**—Eastman Kodak Co. *l*-ascorbic acid was used.

Water was redistilled in an all-Pyrex still.

Oxygen in cylinders (Linde) was used.

Sodium *p*-Phenolsulfonate.—Eastman Kodak Co. sodium *p*-phenolsulfonate dihydrate was recrystallized several times from distilled water, which for the last two recrystallizations had been redistilled as stated above.

All other chemicals were Baker Analytical or General Chemical Company Reagent Grades.

Apparatus and techniques were those described in the preceding papers of this series, using the two-chamber reaction vessel.[2] The temperature was 20.03 ± 0.02°. Each volume read was corrected to a barometric pressure of 760 mm. The reaction mixtures had a volume of 50 ml. The buffers, present in a concentration of 0.20 molar, were monopotassium phosphate, potassium hydrophthalate, sodium acetate, dipotassium phosphate and sodium *p*-phenolsulfonate. They were adjusted to the proper *p*H with nitric acid or potassium hydroxide.

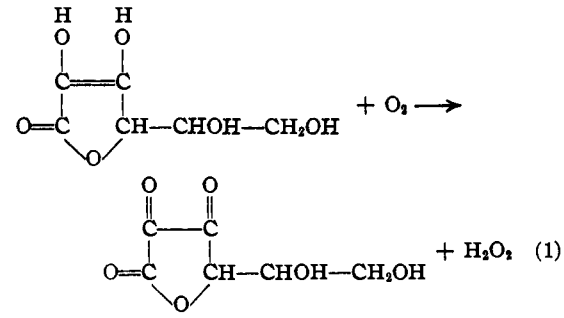
(2) Weissberger, Mainz and Strasser, *Ber.*, **62**, 1942 (1929).

Before the start of the reaction, buffer and cupric nitrate in 45 ml. of water were placed in the lower chamber of the reaction vessel; the ascorbic acid in 5 ml. of water acidulated with 0.2 mmole of nitric acid was in the upper chamber.

Results and Discussion

The experimental results are collected in the table. The headings of the first five columns are the same as those in Table I of the preceding paper.[1] In the sixth column is listed the concentration of the solutions with respect to cupric nitrate as calculated from the amount of the salt added and the total volume of the reaction mixtures (50 ml.).

In column seven is listed the *total oxygen uptake*, a_{ob}, in mole O_2/mole ascorbic acid; a_{ob} is defined as the volume of oxygen absorbed after a time $t = 10\tau$ where τ is the time required for the absorption of 0.5 mole of oxygen per mole of ascorbic acid. If ascorbic acid reacts with oxygen forming dehydroascorbic acid and hydrogen peroxide according to equation 1



(1)

then theoretically one mole of oxygen will be absorbed per mole of ascorbic acid, provided the hydrogen peroxide neither reacts with ascorbic acid nor decomposes to oxygen and water. Either of the latter reactions might lower the total volume of oxygen absorbed to 0.5 mole, while a reaction of the peroxide with dehydroascorbic acid or its decomposition products would not affect this volume. The reaction of hydrogen peroxide with dehydroascorbic acid is very rapid in the

TABLE I

AUTOXIDATION OF ASCORBIC ACID, 0.00800 MOLE/LITER

Buffer 0.200 *M*	Initial *p*H	Final *p*H	P_{O_2}, mm.	Monovalent ascorbate ion, %/100	Metal added mole/l. × 10^5 $Cu(NO_3)_2$	a_{ob}, O_2/H_2A	k^I, min.$^{-1}$ × 10^5	k_1, min.$^{-1}$ × 10^3	k_{Cu}, min.$^{-1}$ × 10^3	k'_{Cu}, min.$^{-1}$
$KHCO_3$	9.32	9.14	740.8	0.9936	20.0	1.12	119	28.2	91	0.092
$KHCO_3$	9.31	9.15	733.0	.9936	20.0	1.11	129	28.2	101	.10
K_2HPO_4	7.49	7.54	730.5	.9995	20.0		170	0.484	170	.17
K_2HPO_4	7.01	7.07	730.3	.9986	20.0		153	.216	153	.15
KH_2PO_4	6.66	6.70	730.3	.9972	20.0		179	.158	179	.18
K_2HPO_4	6.19	6.24	737.4	.9915	20.0		125	.105	125	.13
K_2HPO_4	6.14	6.18	736.1	.9905	40.0	0.77	171	.100	171	
K_2HPO_4	6.12	6.15	736.8	.9901	20.0	.79	134	.0988	134	.13
K_2HPO_4	6.09	6.14	734.7	.9893	12.0	.81	108	.0958	108	
K_2HPO_4	6.09	6.20	733.6	.9893	4.00	.83	54.6	.0958	54.5	
K_2HPO_4	6.12	6.05	733.0	.9901	0.00		3.41	.0988	3.31	
K_2HPO_4	5.62	5.72	739.8	.9693	20.0		111	.0638	111	.12
NaO_2CCH_3	5.08	5.08	733.2	.9007	20.0	.80	90.8	.0398	90.8	.10
NaO_2CCH_3	3.87	3.86	736.2	.3595	20.0	.76	26.0	.0142	26.0	.072
KH_2PO_4	2.59	2.64	738.1	.0286	20.0		2.48	.0080	2.47	.087
$NaO_2SC_6H_4$(p)OH	9.32	9.29	732.9	.9936	20.0		43.0	29.0	14.0	.014
$NaO_2SC_6H_4$(p)OH	8.35	8.36	732.9	.9992	20.0		39.8	3.35	36.4	.036
$NaO_2SC_6H_4$(p)OH	7.95	7.89	734.8	.9996	200.0	.94	153	1.36	152	
$NaO_2SC_6H_4$(p)OH	7.94	7.93	733.1	.9996	160.0	.94	124	1.35	123	
$NaO_2SC_6H_4$(p)OH	7.95	7.89	730.2	.9996	120.0	.95	110	1.36	109	
$NaO_2SC_6H_4$(p)OH	7.94	7.95	728.5	.9996	80.0	.96	83.0	1.35	81.7	
$NaO_2SC_6H_4$(p)OH	7.92	7.88	723.9	.9996	40.0	.96	56.1	1.26	54.8	
$NaO_2SC_6H_4$(p)OH	7.93	7.88	734.4	.9996	20.0	1.00	30.2	1.30	28.9	.029
$NaO_2SC_6H_4$(p)OH	7.91	7.80	735.9	.9996	0.00	1.02	2.02	1.24	0.78	
$NaO_2SC_6H_4$(p)OH	7.87	7.77	736.6	.9996	20.0		33.9	1.13	32.8	.033
$KH(O_2C)_2C_6H_4$	5.42	5.50	740.8	.9521	20.0		72.8	0.0537	72.8	.076
$KH(O_2C)_2C_6H_4$	4.88	4.95	738.8	.8516	20.0		37.7	.0338	37.7	.044
$KH(O_2C)_2C_6H_4$	4.36	4.42	739.5	.6325	20.0		21.0	.0214	21.0	.033
$KH(O_2C)_2C_6H_4$	4.28	4.36	732.7	.5901	20.0		21.8	.0199	21.8	.037
$KH(O_2C)_2C_6H_4$	4.29	4.35	730.9	.5968	40.0		34.6	.0199	34.6	
					$AgNO_3$					
NaO_2CCH_3	5.12	5.17	736.5	.9090	20.0		2.54			
NaO_2CCH_3	5.10	5.08	740.2	.9052	00.0		2.27			

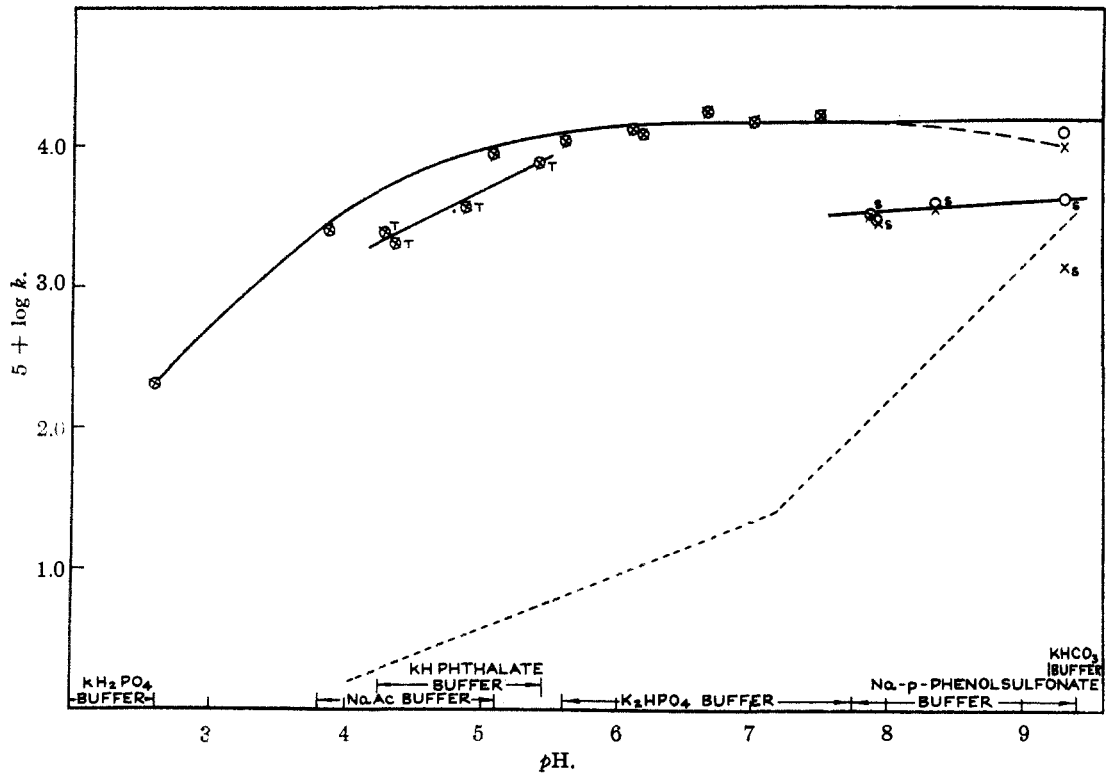


Fig. 1.—O, $5 + \log k^{I}$; ×, $5 + \log k_{Cu}$: . . . . . , $5 + \log k_1$; *T*, $C_6H_4(COO)_2HK$ buffer; *S*, $NaO_3SC_6H_4OH$ buffer.

alkaline range[3] in analogy to the common behavior of α-diketones.[2,4]

In the presence of copper the total uptake at *p*H 7.9 is close to the theoretical of eq. 1. At higher *p*H, a_{ob} is higher, 1.11 mole O_2 per mole of ascorbic acid at *p*H 9.3, presumably because decomposition products of dehydroascorbic acid absorb O_2.[1,5] At *p*H 7.8 to 6.2, the experiments were not observed sufficiently long to obtain a_{ob}. At *p*H 6.12 and down to *p*H 3.9, a_{ob} reaches only 80% of the theoretical value required by eq. 1, indicating that about 40% of the hydrogen peroxide decomposes to O_2 and H_2O, or 20% reacts with the ascorbic acid. Probably both reactions take place; the decomposition of hydrogen peroxide is catalyzed by cupric ion,[6] and the same catalysis has been suggested for the reaction of hydrogen peroxide with ascorbic acid.[7]

The plot of log $(a_{th}-x)$—where a_{th} is the theoretical volume of O_2 required by eq. 1 and x is the oxygen absorbed at the time t—against t is linear up to 80% of the theoretical uptake a_{th}, except for solutions of *p*H 5, which give straight lines for only 50% of the theoretical uptake.[8] This linearity justifies the calculation of a first-order reaction constant, k, by multiplication of the slope of the straight line with −2.303. The value of k corrected to an oxygen pressure of 760 mm. by multiplication with 760/(barometric pressure − P_{H_2O}) during the experiment is k^{I}. P_{H_2O}, the partial pressure of water at 20° is 17.5 mm.

The linearity of log $(a_{th} - x)$ *vs.* t shows in accordance with the literature,[9,1] that k is independent of the *concentration of ascorbic acid.* The dependence of the autoxidation rate on the *oxygen concentration* is reviewed in the introduction. The *dependence of log k^{I} on pH* of solutions to which is added 2×10^{-5} mole/liter of cupric nitrate, is shown in Fig. 1. The experimental points are marked by O. Those obtained in phosphate, acetate and carbonate buffer lie on a smooth curve. The rate in phthalate and *p*-phenolsulfonate buffer is lower than in phosphate, acetate and carbonate at the same *p*H.

The smooth log k^{I}/*p*H curve is discussed first. Barron, DeMeio and Klemperer[9a] as well as Schummer[9b] showed that ascorbic acid reacts

(3) Steinman and Dawson, THIS JOURNAL, **64**, 1212 (1942).

(4) Weitz and Scheffer, *Ber.*, **54**, 2327 (1921).

(5) Borsook, Davenport, Jeffrays and Warner, *J. Biol. Chem.*, **117**, 237 (1937); Dodds, *Univ. of Pittsburgh Bull.*, **37**, 84 (1941).

(6) Von Kiss and Lederer, *Rec. trav. chim.*, **46**, 453 (1927).

(7) Hand and Greisen, THIS JOURNAL, **64**, 358 (1942).

(8) One must wonder whether the experiments by Peterson and Walton, THIS JOURNAL, **65**, 1212 (1943), justify the assumption of an autocatalytic reaction made by these authors. Their results might rather indicate a failure to keep the reaction mixture saturated with oxygen. This will depress the rate in the beginning of a reaction more than later on, because the volume of oxygen reacting per time unit is greatest at the start. For conditions of saturation with oxygen, see Weissberger, Mainz and Strasser, *Ber.*, **62**, 1942 (1929); Weissberger and Thomas, THIS JOURNAL, **64**, 1561 (1942).

(9) (a) Barron, DeMeio and Klemperer, *J. Biol. Chem.*, **112**, 625 (1926); (b) Schummer, *Biochem. Z.*, **304**, 1 (1940); (c) Dekker and Dickinson, THIS JOURNAL, **62**, 2165 (1940).

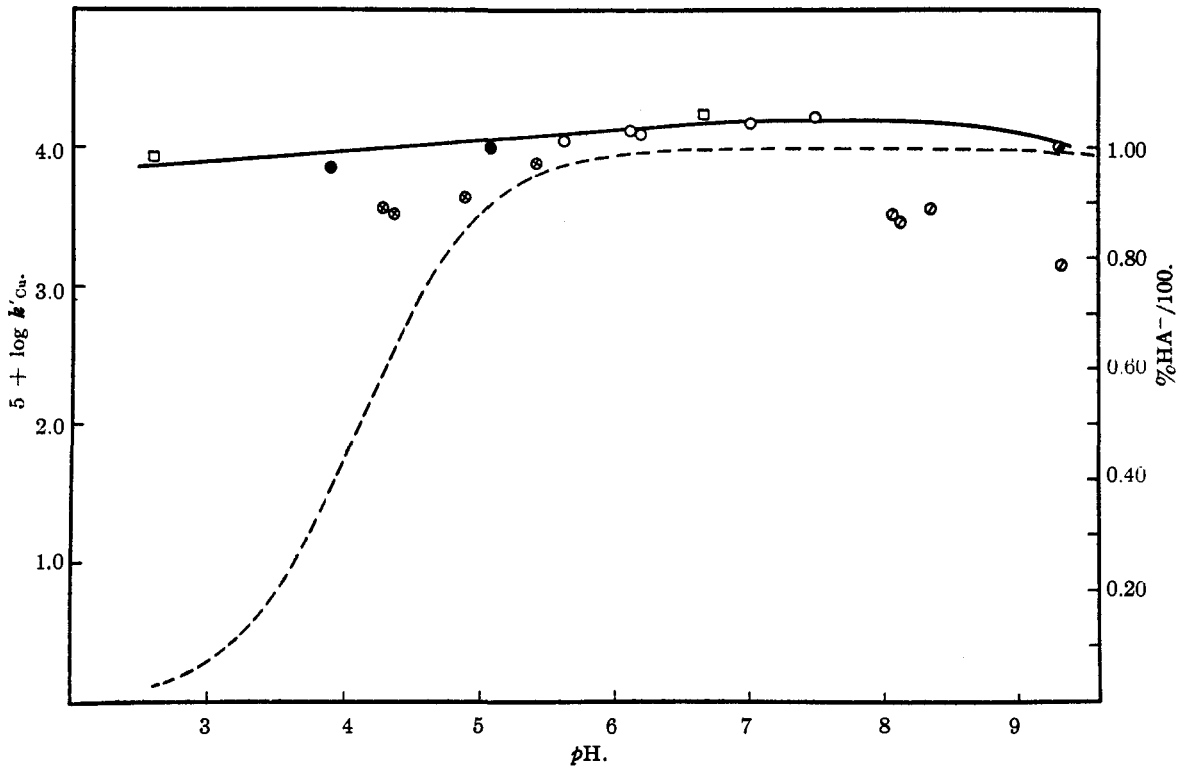


Fig. 2.— ———. 5 + log k'_{Cu}; — — — —, %HA⁻/100; O. K_2HPO_4 buffer; □. KH_2PO_4 buffer; ●, $NaC_2H_3O_2$ buffer; ◑. $KHCO_3$ buffer; ⊕, $NaO_3SC_6H_4OH$ buffer; ⊗, $C_6H_4(COO)_2HK$ buffer.

with oxygen even under conditions which exclude the catalytic action of metals. The rate of this reaction as determined in the preceding paper of this series,[1] is given under k_1 in the table and log k_1 is represented by the dotted line in Fig. 1. If we assume that in the presence of copper the non metal-catalyzed reaction proceeds simultaneously with the copper-catalyzed, the rate of the copper-catalyzed reaction, $k_{Cu} = k^1 - k_1$. At *p*H 2.59 to 7.73, k_1 is negligible in comparison with k^1, but at higher *p*H, log k_{Cu} differs appreciably from log k^1, as shown by Fig. 1, where x denotes log k_{Cu}.

In order to investigate whether copper catalyzes only the autoxidation of the monovalent ion or also that of the un-ionized acid and the divalent ion, we divide k_{Cu} by %HA⁻/100, *i. e.*, by the fraction of the monovalent ion,[1] at the respective *p*H, to obtain k'_{Cu}. The fraction %HA⁻/100 plotted against *p*H gives the dotted curve in Fig. 2, while log k'_{Cu} is represented by O and the solid line. The points corresponding to the smooth curve in Fig. 1 are approximately on a parallel to the abscissa. Such a parallelism should be expected if the *copper affects only the autoxidation of the monovalent ion of ascorbic acid and does not accelerate noticeably the autoxidation of the divalent ion or of the un-ionized acid.* According to these observations, the reactivity of the monovalent ion in the presence of 2×10^{-5} mole/liter of copper, k'_{Cu}, in the *p*H range 2.6 to 9.3 is 0.12 ± 0.03 min.$^{-1}$. It is 10^4 times greater than the reactivity of the monovalent ion in the absence of metal catalysis, k'.[1]

However, it must be noticed that the solid line in Fig. 2, which is drawn through the points corresponding to the smooth curve in Fig. 1, is not strictly straight and parallel to the abscissa, but provides for a flat maximum around *p*H 8. Although no measurements were made between *p*H 7.5 and 9.3 for lack of a suitable buffer, and although the rate at *p*H 9.3 is close to the limit of capacity of our apparatus,[8] this rate was ascertained by repeated measurements, and we believe that the maximum is real. It is readily explained as follows. The added copper, 2×10^{-5} molar, cannot be assumed to be present as atoms or free ions. No measurable solubility of copper atom could be found recorded in the literature. For cupric ion, according to Latimer's data,[10] the concentration of the saturated solution sinks below 2×10^{-5} at *p*H 6.5, and for cuprous ion the drop should occur around *p*H 4. caused in both cases by the precipitation of the respective hydroxides. Saturation phenomena were observed at neither of these *p*H values. On the other hand, cupric ion readily forms complexes with organic hydroxy compounds,[11] and

(10) Latimer, "Oxidation Potentials," Prentice-Hall, New York, N. Y., 1938, pp. 174, 175.

(11) (a) Kahlenberg, *Z. physik. Chem.*, **17**, 577 (1895); (b) F. J. Bates and associates, "Polarimetry, Saccharimetry and the Sugars," National Bureau Standards Circ. 440, 1942, p. 167.

copper which is present in our solutions in its cupric form will be coördinated with the ascorbic acid, *i. e.*, with its molecules and both ionic species. However, since only the monovalent ascorbate ion is the substrate of the catalysis, it may be assumed that the copper coördinated with the monovalent ion is catalytically active to the exclusion of, or in preference to, the copper coordinated with the neutral molecule and the divalent ion. Hence, the latter two species deprive the monovalent ion of some of the catalyst. The autoxidation rate should therefore show a maximum which coincides with the maximum of $\%HA^-/100$, Fig. 2. in agreement with the observations.

The deviation of the autoxidation rate in phthalate and in *p*-phenolsulfonate buffer may likewise be ascribed to a complex formation of these buffers with the copper, and there is little doubt that the inhibition by citrate and pyrophosphate reported by Steinman and Dawson[3] has a similar cause.

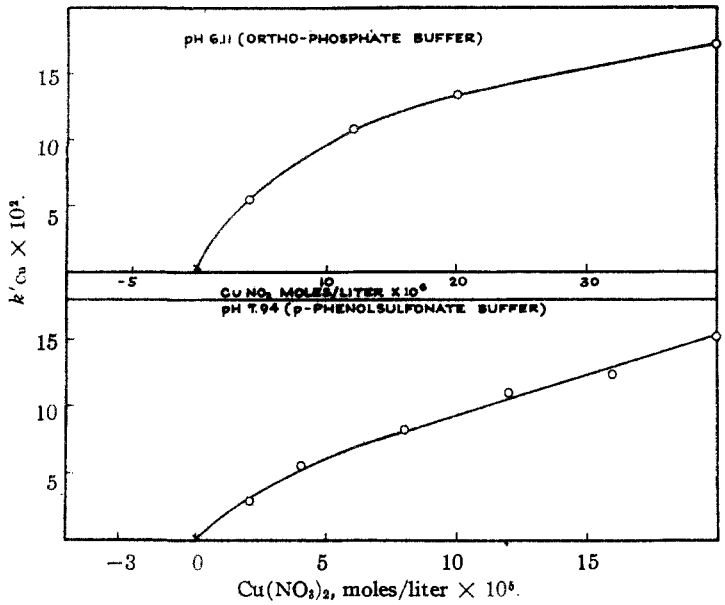


Fig. 3.

There remains to be discussed some scant experiments on the *dependence of k on the copper concentration*. In Fig. 3, k^1 is plotted against the amount of copper added at *p*H 6.11 in phosphate and at *p*H 7.94 in *p*-phenolsulfonate buffer. The reaction rates at the same *p*H in the presence of cyanide and thiocyanate are used as the origin of the coördinates, and the reaction rates in the buffers, without addition of either cyanide and thiocyanate or copper, are marked by *X*. If one draws a smooth curve through all the points and the origin for a given *p*H, one can interpolate the amount of copper which would cause k^1 to be raised from the origin to the value marked by *X*. This for phosphate at *p*H 6.11 is 0.03×10^{-5} and for *p*-phenolsulfonate at *p*H 7.94 is 0.005×10^{-5}. The catalyst present as an impurity of the reagents is therefore considered as negligible against an addition of 2×10^{-5} mole/liter of copper. The function of k^1 *vs.* copper, which is concave toward the abscissa at low concentrations of the metal, becomes a linear function of the latter in the region of about 2×10^{-5} mole/liter of copper present.

In a single experiment at *p*H 5.12 in acetate buffer, it was found that an addition of 2×10^{-5} mole/liter of Ag^+ has no effect which might indicate a catalytic action of the metal on the autoxidation rate of ascorbic acid.

With the information at hand that the monovalent ion is the substrate of the copper catalysis, it is tempting to discuss the mechanism of the latter. To simplify this discussion we disregard the possibility of chain reactions. All the evidence accumulated in the earlier papers of this series agrees with the plausible assumption that the transfer of an electron from a semiquinone ion to O_2 or O_2^-, to form a quinone, is a rapid process. However, the formation of the radical (semiquinone), the first step on the way from a hydroquinone to a quinone, or, more generally, from an enediol to a diketone, can be slow. Thus, the dependence of k'_1 on O_2 indicated that in the autoxidation of the monovalent ascorbate ion in the absence of metals "the formation of an intermediate of semiquinone-like structure" is the rate-determining step.[1] Hence, it is a sufficient reason for the catalytic action of copper in the autoxidation of ascorbic acid, if the metal accelerates the reaction $HA^- \rightarrow A^- + H$.[12] This, as it is written, involving the elimination of hydrogen atom, is most improbable, while the sequence $HA^- \rightarrow HA + e$, $HA \rightleftharpoons H^+ + A^-$ presents a plausible process in which copper ion may act as electron acceptor. Correspondingly, the copper ion should undergo the change $Cu^{++} \rightarrow Cu^+$, or $Cu^+ \rightarrow Cu$. The second alternative is unlikely because it would lead to plating out of copper. On the other hand, Cu^{++}, as mentioned above, will be coördinated with the ascorbic acid. Hence, the monovalent ascorbate ion may change to the semiquinone-like radical by an electron transfer within the complex of Cu^{++} with the monovalent ion, $[Cu^{++}, HA^-] \rightarrow Cu^+$, HA. No indication was found in the literature[11b] for complex formation of Cu^+ with organic hydroxy compounds. Although radicals may

(12) Using the symbol H_2A for ascorbic acid, and, accordingly, A for dehydroascorbic acid, the semiquinone is written as HA and the semiquinone ion as A^-. The latter two species, related to each other by a simple acid ionization, *i. e.*, a fast process, are equivalent kinetically.

behave differently, the unbracketed "complex" is probably unstable, while the liberated Cu^{+} ion is likely to undergo rapid oxidation to Cu^{++}.

Summary

1. The autoxidation rate of *l*-ascorbic acid in the presence of copper (2×10^{-5} mole/liter) is investigated from *p*H 2.59 to 9.31.

2. The results agree with the assumption that in the primary reaction, one mole of dehydroascorbic acid and of hydrogen peroxide is formed from one mole of ascorbic acid and oxygen.

3. The rate is independent of the ascorbic acid concentration, and, as shown in the preceding paper of the series, proportional to the oxygen concentration.

4. At very low copper concentrations, the rate increases faster than the concentration of the metal. At higher concentrations of the latter, the rate increase becomes proportional to the increase in the copper concentration.

5. The dependence of the rate on *p*H in the presence of copper has the appearance of being complex. However, analysis shows that neither the neutral acid nor the divalent ion, but *only the monovalent ion of l-ascorbic acid is the substrate of the copper catalysis*, and that the apparent irregularity in the dependence of the rate on *p*H is caused by complex formation of some of the buffers with the copper catalyst. A concentration of 2×10^{-5} mole/liter of copper, about 4 mg. of $Cu(NO_3)_2$ per liter, increases the reaction rate of the monovalent ascorbate ion by a factor of 10^4.

6. No corresponding effect of silver was found at *p*H 5.12.

7. The mechanism of the catalysis is discussed briefly.

ROCHESTER, NEW YORK RECEIVED FEBRUARY 1, 1944

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF CALIFORNIA AT LOS ANGELES]

The Reaction of Dibromides of Mono-substituted Ethylenes with Potassium Iodide

BY DAVID PRESSMAN AND WILLIAM G. YOUNG

Iodide ion reacts with the dibromide of an olefinic compound to yield the original unsaturated compound, bromide ion and triiodide ion according to equation 1.[1]

$$RCHBrCH_2Br + 3I^- \longrightarrow 2Br^- + I_3^- + RHC{=}CH_2 \quad (1)$$

The reaction proceeds first order with respect to the dibromide concentration and also with respect to the iodide ion concentration in 99% methanol solution and is practically independent of the triiodide ion concentration.

We have shown that in the reactions of dibromides of *cis* and *trans* olefins with potassium iodide the reaction is slower for the dibromide from the *cis* olefin[2] and that the olefin produced is in its original stereoform in the case of the 2-butene dibromides.[3] The reaction takes place presumably through the attack by an iodide ion to remove a positive bromine atom as iodine bromide while, simultaneously, the electron pair which is left unshared by this removal attacks the carbon face opposite the remaining bromine atom forming a double bond and liberating a negative bromide ion.[3]

Our purpose in this research was to determine the reactivity of various mono-substituted ethylene dibromides with iodide ion. The reactions were studied in 99% methanol at two or more temperatures.

(1) R. T. Dillon, THIS JOURNAL, 54, 952 (1932).

(2) W. G. Young, D. Pressman and C. D. Coryell, *ibid.*, 61, 1640 (1939).

(3) S. Winstein, D. Pressman and W. G. Young, *ibid.*, 61, 1645 (1939).

Experimental

Rates of Reaction.—The rate constants were obtained graphically by the use of equation 2

$$d \log_{10} \frac{1 - 3b\varphi/a}{1 - \varphi} \Big/ dt = \frac{a - 3b}{2.303} k_{obs.} \quad (2)$$

where a and b are the initial iodide and dibromide concentrations respectively, φ is the fraction of dibromide reacted and t is the time in hours. The following corrections were made as discussed previously[2]: (a) correction to standard temperature of 45.00, 60.00, 75.00, 80.00 or 85.00°, (b) correction for activity of solvent (methanol preparations I, II, III are the same as those used previously[2]). (c) correction for salt effect, and (d) correction for solvent expansion.[4]

Preparation of Materials

1-Pentene dibromide was prepared by mixing slowly at 0° bromine with the 1-pentene obtained from ethylmagnesium bromide and allyl bromide. The product was fractionated through a Weston column and the fraction boiling at 84.5–85.5° at 15 mm. was used.

Acrylic Acid Dibromide.—The Eastman Kodak Co. product melting at 59–61° was used.

Styrene dibromide was prepared from styrene and bromine in carbon disulfide. The solvent was evaporated and the product recrystallized from alcohol: m. p. 74.0–74.5°.

Allylbenzene dibromide was prepared by brominating, in carbon tetrachloride, allylbenzene obtained from allyl bromide and phenylmagnesium bromide. The product was fractionated and the fraction boiling at 126° at 2 mm. was used.

Allyl Alcohol Dibromide.—The Eastman Kodak Co. product was refractionated and the fraction boiling 113–114° at 13 mm. was used.

(4) Corrections of 3.0, 4.3, 6.3, 7.6 and 8.1% were made at temperatures 45, 60, 75, 80 and 90°, respectively; (see ref. 2) Landolt-Börnstein, "Tabellen," Verlag von Julius Springer, Berlin, 1923, Vol. I, p. 278.