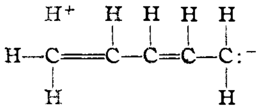
show that the *cis* structure must predominate largely over the *trans*. If the 2-methylbutadiene moment value 0.38 is high by as much as 0.10, which is not impossible, the observed 2,3-dimethylbutadiene moment would agree within its experimental error with the value calculated for the *cis* form. This establishment of the large predominance of the *cis* form agrees with the conclusions of Mulliken[8] that spectroscopic results look almost as if 2,3-dimethylbutadiene were pure *cis*.

In 1-methylbutadiene, *trans*-piperylene, polarity should arise from polar structures analogous to those which have been proposed for propylene and 2-methylbutadiene, but here the negative charge, instead of being displaced three carbon atoms away from the methyl hydrogens is displaced five carbons away to give



$$\begin{array}{ccccccccccc} & & \mathrm{H^+} & & \mathrm{H} & & \mathrm{H} & & \mathrm{H} & & \mathrm{H} \\ & & & & | & & | & & | & & | \\ \mathrm{H} & - & \mathrm{C} & = & \mathrm{C} & - & \mathrm{C} & = & \mathrm{C} & - & \mathrm{C}:^- \\ & & | & & & & & & & & | \\ & & \mathrm{H} & & & & & & & & \mathrm{H} \end{array}$$

Since three such structures are the principal source of the moment of the molecule as in the cases of propylene and 2-methylbutadiene, the moment of the molecule should be to that of 2-methylbutadiene approximately as the charge separation in the 1-methyl is to that in the 2-methyl molecule. Measurement of the molecular models shows that the ratio of these distances is approximately 1.5 if 1-methylbutadiene is *cis* with respect to the central single bond and 1.8 if it has the more probable[8] *trans* structure. The fact that the ratio of the two moment values in Table II is 1.8 gives striking evidence in support of the validity of this theory of hyperconjugation as applied to unsaturated compounds.

Summary

The dielectric constants of the vapors of butadiene, 1-methyl-, 2-methyl- and 2,3-dimethylbutadiene have been measured and used to calculate the dipole moments of the molecules. The moment of 2,3-dimethylbutadiene shows that the molecules are largely, if not entirely, in a *cis* form with respect to the central C–C bond. The moment values give quantitative evidence in support of the theory of hyperconjugation, which requires positive charges on the methyl hydrogens and a negative charge on a terminal carbon.

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[COMMUNICATION NO. 940 FROM THE KODAK RESEARCH LABORATORIES]

Oxidation Processes. XVI.[1] The Autoxidation of Ascorbic Acid

BY A. WEISSBERGER, J. E. LUVALLE AND D. S. THOMAS, JR.

α-Ketols form with molecular oxygen the corresponding diketones and hydrogen peroxide

$$\mathrm{R{-}CHOH{-}CO{-}R} + \mathrm{O_2} \longrightarrow \mathrm{R{-}CO{-}CO{-}R} + \mathrm{H_2O_2}^{2} \quad (1)$$

The rates of this reaction and of the oxidation of α-ketols with Fehling solution[3] are ***proportional to the hydroxyl-ion concentration of the solutions***, and it was suggested that the rate-determining phase is the enolization of the ketol to the enediol ion[2]

$$\mathrm{R{-}CHOH{-}CO{-}R} + \mathrm{OH^-} \rightleftarrows \mathrm{R{-}COH{=}CO^-{-}R} + \mathrm{H_2O} \quad (2)$$

This suggestion was confirmed by the observation that under identical conditions of alkalinity, *d*-benzoin, in the absence of oxygen, is racemized at the *same rate* at which benzoin is oxidized, when shaken with oxygen.[4] When the oxygen supply is scant, an intensely colored intermediate appears, the free radical R—COH—CO—R.[2a] This indicates that the oxidation of the enolized compound proceeds in two steps[5] by way of the free radical. The ionic species reacting in the first step may be the monovalent ion, (3), or the divalent ion (4), which is formed in the equilibrium (5).

$$\mathrm{R{-}COH{=}CO^-{-}R} + \mathrm{O_2}(\text{or } \mathrm{O_2^-}) \longrightarrow \mathrm{R{-}COH{-}CO{-}R} + \mathrm{O_2^-}(\text{or } \mathrm{O_2^{--}}) \quad (3)$$

$$\mathrm{R{-}CO^-{=}CO^-{-}R} + \mathrm{O_2}(\text{or } \mathrm{O_2^-}) \longrightarrow \mathrm{R{-}CO^-{=}CO{-}R} + \mathrm{O_2^-}(\text{or } \mathrm{O_2^{--}}) \quad (4)$$

$$\mathrm{R{-}COH{-}CO^-{-}R} + \mathrm{OH^-} \rightleftarrows \mathrm{R{-}CO^-{=}CO^-{-}R} + \mathrm{H_2O} \quad (5)$$

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[1] Part XV, Weissberger, Thomas and LuValle, THIS JOURNAL, **65**, 1489 (1943).

[2] (a) Weissberger, Mainz and Strasser, *Ber.*, **62**, 1942 (1929); (b) Weissberger, Strasser, Mainz and Schwarze, *Ann.*, **478**, 112 (1930).

[3] Weissberger, Schwarze and Mains, *Ann.*, **481**, 68 (1930).

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

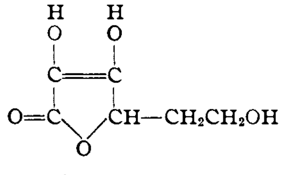
[5] Michaelis and Fletcher, THIS JOURNAL, **59**, 1246 (1937).

It might be argued that, according to (4), the rate of the oxygen absorption should depend on a higher power of $[OH^-]$ than the first, because the hydroxyl ion reacts in both (2) and (5). However, at the high pH (> 12) of our measurements, practically all of the enolized ketol may exist as the doubly-charged ion. In this case, a further increase of pH would not appreciably change the concentration of the doubly-charged ion, and the rate of the over-all reaction would depend linearly on $[OH^-]$, although the doubly-charged ion is the reactive species.

The possibility of an autoxidation of a singly-charged enolate ion is indicated by the autoxidation of benzoin methyl ether[6] and of desylamine,[5] which are both monobasic. If we consider the aromatic *o*- and *p*-dihydroxybenzenes as enediols,[7] the linear dependence of the autoxidation of catechol on the pH,[8] and the autoxidation of the monomethyl ethers of hydroquinone and of durohydroquinone[9] may be regarded as further evidence for the reactivity of singly-charged enediol ions. On the other hand, the doubly-charged tetrachlorodihydroxybenzene ion autoxidizes rapidly, while the singly-charged ion is relatively stable in an atmosphere of oxygen.[10] Furthermore, the dependence of the autoxidation rate of durohydroquinone and hydroquinone on the pH[9] shows that the divalent ions are the reactive ionic species. Only a comparatively small reactivity of the monovalent hydroquinone ion may be indicated by a slight deviation from the square relation.[9]

In the present work, we have attempted to get more information about the relative autoxidation rates of monovalent and divalent ions. The difficulty in observing a reaction of one ionic species taking place beside that of the other is obviously greater the smaller the difference between the two ionization constants. With hydroquinone, the two ionization constants differ only by a factor of 10^2 (pK_1 9.8,[11] pK_2 11.4[12]), and the doubly-charged ion is always present in significant concentration when the singly-charged ion occurs. Of catechol, only the first ionization constant is known ($pK_1 \times 9.1$).[8] With this compound, because of the proximity of the ionizing groups to each other, pK_1 and pK_2 can be expected to be further apart than with hydroquinone. This fact, together with a rather high reactivity of the singly-charged ion, would explain the difference in the pH dependence of the autoxidation of catechol and of hydroquinone, just mentioned.

The ionization constants of the enediol ascorbic acid differ by more than a factor of 10^7, pK_1 4.12, pK_2 11.51.[13] This compound, therefore, appeared to offer a chance to observe the oxidation of the different ionic species as separate entities. In the following, the neutral molecules of *l*-ascorbic acid are symbolized by H_2A, and the ions by HA^- and A^{--}, respectively. The fractions of the ions are calculated according to (6) and plotted against the pH in Fig. 1



$$\text{Fraction of HA}^- = \frac{K_1(1/H^+)}{1 + K_1(1/H^+)} - \frac{K_2(1/H^+)}{1 + K_2(1/H^+)}$$
$$\text{Fraction of A}^{--} = \frac{K_1(1/H^+)}{1 + K_1(1/H^+)} \cdot \frac{K_2(1/H^+)}{1 + K_2(1/H^+)} \qquad (6)$$

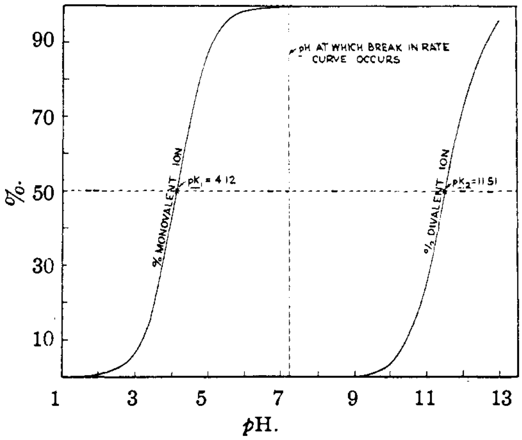


Fig. 1.

Materials and Methods

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

Water was redistilled in an all-Pyrex still.

Oxygen in cylinders (Linde) was used, unless noted otherwise.

All other chemicals were Baker's Analytical or General Chemical Company Reagent grades.

Aqueous solutions were used in all experiments.

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[6] James and Weissberger. THIS JOURNAL, **59**, 2040 (1937).

[7] I. Ostromislensky (private communication); Kenner, *Nature*, **147**, 482 (1941).

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

[9] James, Snell and Weissberger, *ibid.*, **60**, 2084 (1938).

[10] Weissberger, *Ber.*, **65**, 1815 (1932).

[11] Cameron, *J. Phys. Chem.*, **42**, 1217 (1938).

[12] Sheppard, *Trans. Am. Electrochem. Soc.*, **39**, 429 (1921); LaMer and Parson, *J. Biol. Chem.*, **57**, 613 (1927).

[13] Kumler and Daniels, THIS JOURNAL, **57**, 1929 (1935).

The apparatus and the techniques were those described in the preceding papers of this series. The temperature was 20.03 ± 0.02°. Each volume read was corrected to a barometric pressure of 760 mm. The reaction mixtures, unless otherwise stated, had a volume of 50 ml. The buffer concentration was 0.2 molar. The buffers used were monopotassium phosphate, potassium hydrophthalate, dipotassium phosphate, and sodium *p*-phenolsulfonate. They were adjusted to the right *p*H with nitric acid or with potassium hydroxide.

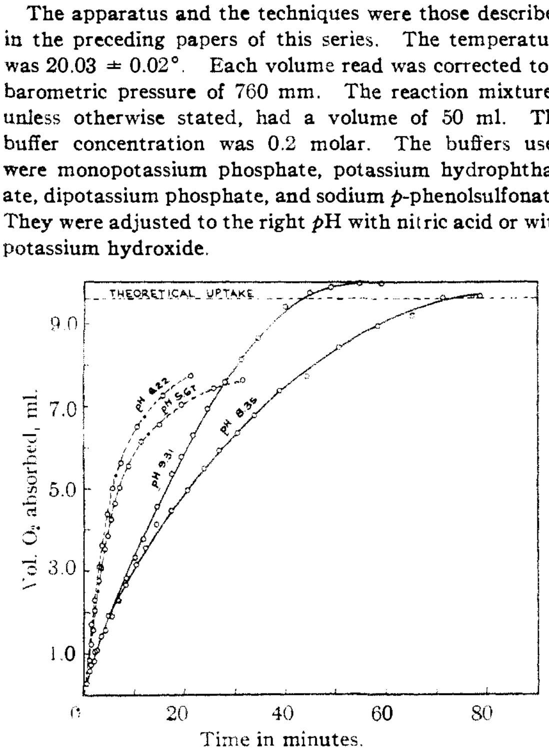

Fig. 2. —O—O— Sulfonate buffer; ··O··O·· phosphate buffer. In the absence of inhibitors the influence of buffers on the reaction rates is not restricted to the *p*H effect. The additional influence may be caused by varying amounts of metals, or by some other factor

Results and Discussion

The literature on the autoxidation of ascorbic acid does not give the information desired. It shows clearly that consistent results over a wide *p*H range can be expected only if the catalysis by metals, particularly copper and iron, is either avoided or controlled.[14] In order to suppress the catalysis by metals in our experiments, cyanide and thiocyanate were added to the reacting solutions to make them 0.0010 *N* and 0.0034 *N*, respectively.[14a]

Some discussion is necessary concerning the total volume of oxygen which is absorbed by a given amount of ascorbic acid and enters into the calculation of the rate constants. For reactions of the type (1), this volume should be 1 mole of O_2/mole of ascorbic acid.[14e,f] Actually, the volumes absorbed at *p*H 7 and above are higher than this theoretical volume *a*, because the primary oxidation products of ascorbic acid react further with oxygen.[15] The decomposition of the hydrogen peroxide,[14a] or the reaction of the hydrogen peroxide with ascorbic acid, would have the opposite effect. Above *p*H 7 most of the peroxide appears to be consumed in a rapid reaction[2a] with dehydroascorbic acid,[14e,f] and, possibly, with other oxidation products of ascorbic acid. In the acid region, it was not convenient to observe many experiments long enough to draw conclusions on the total oxygen absorption, because of the slowness of the reactions. However, Fig. 2 shows experiments in which 0.001 mole of cupric nitrate, but no inhibitor, was added, together with measurements in the alkaline region for comparison. The "end-volume" sinks, in agreement with Steinman and Dawson,[14f] with lower *p*H.

The deficit in the oxygen absorption, as compared with the theoretical, below *p*H 7, is substantially smaller in the absence of copper and the presence of cyanide and thiocyanate, than in the copper-catalyzed reaction. Moreover, the reactions which cause the deviations from *a* appear to become prevalent in the later stages of the runs. Therefore, the theoretical volume *a* was used in the calculation of all our experiments. When the log $(a - x)$ values were plotted against the time, straight lines resulted in the alkaline region up to above 80%, in the acid region up to at least 50%, and in many cases to more than 60%, of the theoretical turnover, *a*. This linearity, which is shown in Fig. 3 for a number of representative experiments, justifies the general

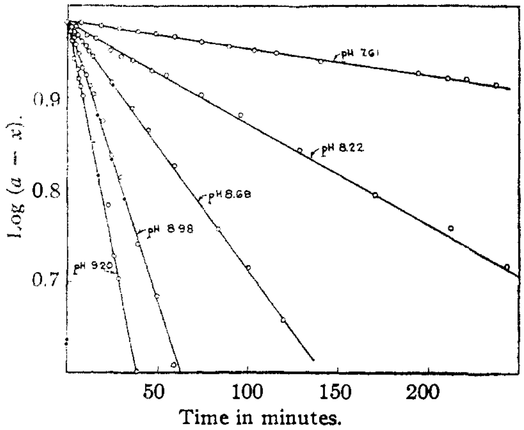

Fig. 3.

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[14] (a) Barron, DeMeio and Klemperer, *J. Biol. Chem.*, **112**, 625 (1936); (b) Dekker and Dickinson, THIS JOURNAL, **62**, 2165 (1940); (c) Schummer, *Biochem. Z.*, **304**, 1 (1940); (d) Sinohara, *J. Chem. Soc. Japan*, **61**, 733 (1940); (e) Hand and Greisen, THIS JOURNAL, **64**, 358 (1942); (f) Steinman and Dawson, *ibid.*, **64**, 1212 (1942); (g) Nystkowski, *Nature*, **150**, 234 (1942); (h) Silverblatt, Robinson and King, THIS JOURNAL, **65**, 137 (1943).

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

TABLE I

AUTOXIDATION OF ASCORBIC ACID IN THE PRESENCE OF CYANIDE (0.0010 *M*) AND THIOCYANATE (0.00034 *M*)

Buffer 0.20 *M*	Initial *p*H	Final *p*H	P_{O_2}, mm.	Ascorbic acid, mole/l.	Monovalent ascorbate ion, %/100	Divalent ascorbate ion, %/100	$k \times 10^4$ min.$^{-1}$	$k_1 \times 10^4$ min.$^{-1}$	k_1'' min.$^{-1}$	$k_1' \times 10^5$ min.$^{-1}$
p-Phenolsulfonate	9.21	9.18	728.5	0.00800	0.9951	4.85×10^{-3}	219	228	4.7	
	9.21	9.18	728.2	.00800	.9952	4.76	211	219	4.6	
	9.19	9.22	740.1	.00400	.9951	4.85	239	243	5.1	
p-Phenolsulfonate[a]	9.17	9.13	154.2	.00800	.9957	4.33	46	227		
p-Phenolsulfonate	9.11	9.10	741.6	.0160	.9961	3.96	174	178	4.5	
	8.95	9.01	734.4	.00800	.9971	2.93	136	141	4.8	
	8.95	9.01	740.1	.00800	.9971	2.93	147	151	5.2	
K_2HPO_4[b]	8.71	8.79	740.0	.0160	.9983	1.74	105	108		
p-Phenolsulfonate	8.68	8.69	731.0	.00800	.9984	1.47	61.2	63.5	4.3	
	8.21	8.24	729.5	.00800	.9994	5.11×10^{-4}	24.9	25.8	5.0	
	7.97	8.01	734.6	.00800	.9996	3.02	15.2	15.8	5.2	
p-Phenolsulfonate[a]	7.82	7.75	154.0	.0200	.9996	1.85	1.73	8.54		
K_2HPO_4	7.61	7.61	738.2	.0160	.9996	1.25	6.81	7.01		
K_2HPO_4	7.58	7.63	737.5	.0160	.9996	1.25	6.32	6.51		
K_2HPO_4	7.41	7.40	732.8	.0300	.9994	7.99×10^{-5}	3.61	3.75		
K_2HPO_4	7.16	7.20	718.3	.0444	.9992	4.65	2.42	2.56		
K_2HPO_4[c]	7.10	7.12	739.0	.0160	.9990	3.98	3.47	3.58		
K_2HPO_4[a]	7.08	7.04	154.0	.0200	.9989	3.52	0.93	4.56		
K_2HPO_4	7.06	6.98	736.1	.0200	.9988	3.23	2.94	3.03		
K_2HPO_4[a]	7.00	7.03	154.0	.0200	.9988	3.23	0.985	4.85		
K_2HPO_4	6.88	6.91	736.2	.0200	.9983	2.44	1.84	1.89		7.2
K_2HPO_4	6.47	6.51	723.1	.0500	.9956	9.52×10^{-6}	1.39	1.46		10.1
K_2HPO_4[d]	5.84	5.99	744.5	.00800	.9840	2.45	1210	1240		
K_2HPO_4[a,d]	5.86	5.93	154.5	.00800	.9836	2.39	388	1670		
K_2HPO_4	5.80	5.74	736.1	.0200	.9781	1.78	1.20	1.24		
K_2HPO_4[a]	5.79	5.79	154.5	.0200	.9790	1.86	0.561	2.76		
K_2HPO_4	5.27	5.30	712.0	.1000	.9350	5.47×10^{-7}	.461	0.498		5.1
K_2HPO_4	5.14	5.19	728.7	.0500	.9160	4.08	.415	.431		4.5
K_2HPO_4	4.70	4.72	733.5	.0500	.7940	1.25	.288	.299		3.4

[a] Air over solution instead of oxygen. [b] Cyanide, 0.10 *M*; thiocyanate, 0.0034 *M*. [c] Cyanide, 0.010 *M*, thiocyanate, 0.0034 *M*. [d] No cyanide and thiocyanate; cupric nitrate, 2×10^{-5} *M*.

use of *a* in the calculations. Multiplication of the slopes of the straight lines by −2.303 gives the first-order reaction constants *k*, of Table I.

These constants, in accordance with the literature, are independent of the *concentration of ascorbic acid*.[14a,b,c,h] In the alkaline region, the reaction rate is proportional to the *partial pressure of oxygen*,[14a] when the latter is reduced from about 760 mm. to about 150 mm. by using air. The rate constants k_1 are corrected to an oxygen pressure of 760 mm. by multiplication with 760/partial pressure of oxygen in the experiment. Around the neutral point and in the acid region, the reaction rate varies with a lower power of the oxygen pressure than 1 (see below). However, in view of the relatively small deviations from 760 mm. in the runs with pure oxygen at atmospheric pressure, k_1 was calculated in the same way in the acid region as in the alkaline.

The dependence of k_1 on the *concentration of hydrogen ion* is shown by Fig. 4. The slope of 1.02 at *p*H > 7.2 reveals a linear proportionality of the reaction rate to the hydroxyl-ion concen-

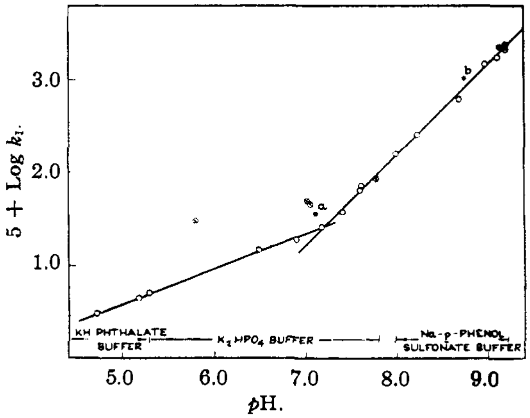

Fig. 4.—○, O_2, Cyanide 0.0010 *M*; thiocyanate, 0.0034 *M*; ●, O_2, (a) cyanide, 0.010 *M*; thiocyanate, 0.0034 *M*; (b) cyanide, 0.100 *M*; thiocyanate, 0.034 *M*; ⊗, air, cyanide 0.0010 *M*; thiocyanate, 0.0034 *M*.

tration. It is obvious from Fig. 1 that at *p*H 7.2 practically all of the ascorbic acid is present as the monovalent ion. Hence, the slope of 1, above *p*H 7.2, shows that the divalent ion is responsible for the oxygen absorption in this *p*H region. The reactivity of the divalent ion with oxygen at atmospheric pressure, $k_1'' = k_1$/fraction of A^{--}, taken between *p*H 7.9 and 9.2, has the mean value 4.9.

Below *p*H 7.2, the slope of the k_1, *p*H curve is 0.38. To interpret this slope, we assume that besides the divalent ion of ascorbic acid, the monovalent ion participates in the oxygen absorption. If the reactivity of the monovalent ion is called k_1', then

$$100k_1 = k_1'(\%\ A^-) + k_1''(\%\ A^{--}) \qquad (7)$$

With the fractions of the ionic species calculated according to (6), and k'' given above, values for k' are obtained which, as shown in the last column of the table, are of the order of 5×10^{-5}. These values and their constancy are in good agreement with the suggestion that the monovalent ion of *l*-ascorbic acid reacts with molecular oxygen at a finite rate. The linearity of the *p*H dependence below *p*H 7.2 is considered as fortuitous. It must be kept in mind that all measurements below *p*H 7.2 were made in the shoulder region of the per cent. monovalent ion curve in Fig. 1, where the divalent ion participates increasingly in the autoxidation. At lower *p*H, the slope of the curve in Fig. 4 should approach 1, provided that the neutral molecule of the ascorbic acid does not react with oxygen. Unfortunately, no measurements could be made below *p*H 4.7 because of the evolution of hydrogen cyanide.

The question arises whether or not the observed reactivities of the monovalent and divalent ion are caused by a catalytic action of metals. Buffers of different kinds were used, as noted in Fig. 4, without any effect other than that explained above with the change in *p*H. This makes a metal catalysis unlikely, because the contaminating metals vary with the buffers, and the form in which the metals are present can be expected to vary with the *p*H. Moreover, the absence of the most powerful catalysis by copper,[14a,16] was corroborated by experiments in which the cyanide concentration was raised from 0.001 to 0.01 and 0.1 mole/liter. As shown in Fig. 4, this increase does not lower the reaction rates, at *p*H 7.11 and 8.75, respectively. Actually, the rates are even higher than with the lowest cyanide concentration, presumably because of the increase in the ionic strength of the solutions.

The reaction rates with air are marked by ⊗ in Fig. 4. The proportionality to the oxygen pressure which is obvious in the alkaline solutions breaks down in the neutral region, and the deviation increases with sinking *p*H. There is no reason to assume a failure of the systems to obey Henry's law. The reaction mechanism rather appears, at lower *p*H, to include a step which is independent of the oxygen concentration and sufficiently slow to affect the rate of the over-all reaction. Since we know, from the experiments above *p*H 8, that the reaction rate of the divalent ion is proportional to the oxygen concentration, the reactivity of the divalent ion with oxygen at the partial pressure in air can be calculated as $4.9 \times 21/100 = 1.03$. With this value, the reactivity of the monovalent ion with oxygen at the partial pressure in air, $k'_{(\mathrm{air})}$, follows from (8).

$$\frac{\%A^{--}}{100} \times 1.03 + \frac{\%A^-}{100} \times k'_{(\mathrm{air})} = k_{(\mathrm{air})} \qquad (8)$$

The values for $k'_{(\mathrm{air})}$ at *p*H 7.08, 7.00 and 5.79 are 5.7×10^{-5}, 6.5×10^{-5} and 5.6×10^{-5}, respectively. Comparison with the values of k_1' in the table shows that the reactivity of the monovalent ion of *l*-ascorbic acid with oxygen, in the presence of cyanide and thiocyanate, is independent of the oxygen pressure, when the latter varies between 1 and 0.21 atmosphere. The monovalent ion must undergo some slow process before it reacts with molecular oxygen. This rate-determining step may be the formation of an intermediate of semiquinone-like structure from the monovalent ion and dehydroascorbic acid, and may be similar to the reactions responsible for the quinone catalyses described in earlier papers of this series.[1] Indications of very brief, and therefore not quite definitely established, induction periods in several runs at low *p*H would agree with this assumption.

In the metal-catalyzed oxidation, the slow process just mentioned is overcome by the action of the catalyst. Dekker and Dickinson[14b] assume that an intermediate of semiquinone-like structure is formed through oxidation of ascorbate by cupric ion. The reaction rate in neutral and acid solutions in the presence of copper may therefore be proportional to the

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(16) Euler, *Z. physik. Chem.*, **217**, 1 (1933); Euler, *Ark. f. Kemi.*, **A11**, Nr. 12 (1933); Mawson, *Biochem. J.*, **29**, 569 (1935); Killie and Zilva, *ibid.*, **29**, 1028 (1935).

oxygen concentration. Barron, DeMeio and Klemperer[14a] report experiments at *p*H 7.04 in which the oxidation of ascorbic acid in the presence of copper is measured with air and with a nitrogen–oxygen mixture containing 5% O_2. The $O_{2\text{absorbed}}$, time curves of both reactions are given in the paper. When the time values of the reaction with 5% O_2 are divided by 21/5, the resulting curve coincides with that of the reaction with air. Likewise, when our experiments in the presence of copper at *p*H 5.84 and 5.86, with oxygen and with air, respectively, are plotted, multiplying the times of the latter run by 0.21, the $O_{2\text{absorbed}}$, time curves coincide up to a turnover of more than 50% of *a*. Afterwards, the reaction with air falls back behind the reaction with oxygen, because the former approaches a smaller end-volume than the latter. In the reaction with air, more time is available for the progress of the end-volume reducing reactions of the hydrogen peroxide. The coincidence of the curves at *p*H 7.04 and 5.85, respectively, demonstrates that the rate of the copper-catalyzed reaction in neutral and acid solutions is proportional to the partial pressure of oxygen, in agreement with the above suggestion. The different dependence of the reaction rate on the oxygen pressure in the absence and the presence of copper and cyanide, respectively, furnishes additional evidence for the absence of a copper catalysis in the reactions containing cyanide and thiocyanate at low *p*H.

In view of the great difference in the specific reactivity of the monovalent and the divalent ion of ascorbic acid, a suggestion may be made concerning the reactive ionic species in the autoxidation of α-ketols, specifically of benzoin. It was shown that, with about 10^{-1} *N* sodium methylate in methanol, benzoin absorbs oxygen at the same rate at which *d*-benzoin is racemized, In the presence of oxygen of atmospheric pressure, the reaction of the enolized benzoin with oxygen is so fast that no ketization can be detected, *i. e.*, (2) proceeds only from left to right. To give this effect, the reactive ionic species must have an oxidation rate which is at least ten times greater than the rate of the enolization. With an enolization rate of the order 10^{-1}, the reactive ionic species should therefore have a *k* of at least unity. If we disregard solvent effects, and assume that the reactivity of the ions of diphenylenediol (enolized benzoin) is not several orders of magnitude higher than that of the corresponding ascorbate ions, the reactivity of the monovalent diphenylenediolate ion would be insufficient for the suppression of the ketization. We are inclined to believe that, unless a metal catalysis increases the reaction rate of the singly-charged ion, the species reacting with oxygen in the autoxidation of benzoin is the doubly-charged enediolate ion.

Summary

The autoxidation rate of *l*-ascorbic acid is investigated between *p*H 4.7 and 9.2, in the presence of cyanide and thiocyanate, to suppress the catalytic action of metals.

The reaction obeys the first-order law with respect to the ascorbic acid.

The dependence of the reaction rate on the *p*H shows that both the singly- and the doubly-charged anions of *l*-ascorbic acid enter into the reaction. The reaction rates at 20° with oxygen of 760 mm. pressure are of the order of 5×10^{-5} and 5, respectively.

The reaction rate of the doubly-charged ion is proportional to the partial pressure of the oxygen.

The reaction rate of the singly-charged ion is independent of the oxygen pressure in the region investigated, the rate being controlled by a step not involving oxygen. The rate of the copper-catalyzed oxidation is proportional to the oxygen concentration in the neutral and acid regions.

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