from liquid air temperature by placing it in dry-ice. As the ketene and alcohol react the heat of the reaction may cause it to get out of control; if this occurs liquid air can be placed in the well W to avoid loss of products. The contents of the trap were distilled and the ethyl acetate content determined by saponification with standard alkali. Our method was checked by a number of blank runs in which we proved that the dimer does not react, under our conditions, with ethyl alcohol to form a volatile ester. In all experiments a weight balance was obtained by comparing the weight of dimer taken with the weight recovered plus the ketene formed. The two weights checked within experimental error and no methane, ethylene or carbon monoxide was found in any of the runs. The experimental results are shown in Table II.

TABLE II

THE THERMAL DECOMPOSITION OF DIKETENE

	I	II	III	IV
Moles diketene used	0.798	0.604	0.478	0.534
Moles diketene recovered	.750	.524	.323	.237
Moles ketene produced	.082	.140	.301	.568
Pressure ±1.0 mm.	9.0	8.7	10.0	9.7
Duration of run, seconds	1650	1280	1110	1340
Contact time, sec.	0.036	0.033	0.039	0.039
Temp., °C. ±8°	410	460	505	548
Decomposed, %	5.14	11.6	31.3	53.2

Summary

1. Pure liquid diketene has been examined by the method of aseptic distillation and found to consist of a single substance.

2. In the vapor state, diketene decomposes quantitatively into ketene. No substances such as methylacetylene, allene or carbon dioxide are formed even in traces. A test for free radicals, using tellurium mirrors, was negative.

3. On the basis of the principle of least motion, we have concluded that the cyclobutanedione formula is the only one that is consistent with our vapor state experiments.

4. Reactions of diketene in condensed systems do not seem to be conclusive in determining its structure. Possibly distortion of the highly resonating diketene molecules by the microscopic fields of the solvent may actually change the structure from that present in the gas phase.

5. The high dipole moment, 3.53, of gaseous diketene appears to rule out the cyclobutanedione formula in spite of the evidence from our vapor state experiments.

WASHINGTON, D. C. RECEIVED APRIL 14, 1943

[CONTRIBUTION FROM THE DIVISIONS OF ANIMAL HUSBANDRY AND CHEMISTRY, COLLEGE OF AGRICULTURE, UNIVERSITY OF CALIFORNIA]

Absorption of Oxygen by Glutathione in Alkaline Solutions. II. Kinetics of the Reaction at *p*H 13

BY M. B. YOUNG AND H. A. YOUNG

It has been shown[1] that, in the presence of a copper salt as catalyst and at a *p*H of 13, the quantity of oxygen absorbed in the reaction between glutathione and oxygen indicates that the product formed is primarily the salt of the sulfinic acid. A continuation of the discussion of the factors influencing the rate of this reaction and the presentation of the rate law and a possible mechanism follow.

Experimental

The experiments were carried out in the Warburg apparatus at 37°. The procedure was similar to that of previous experiments[1] except that it proved more convenient to place 4 cc. of the sodium hydroxide–copper sulfate mixture in the main compartment of the Warburg flask and 1 cc. of glutathione solution in the side arm. Upon mixing, the fine suspension of copper hydroxide dissolved immediately in the glutathione. As before, the oxygen absorption was measured at constant volume. Since only about 5% of the total available oxygen was used during the course of any one experiment, the oxygen pressure remained essentially constant.

The reaction was studied at *p*H 13 to 13.3 with glutathione concentration varying from 0.00110 to 0.00440 molar, copper sulfate concentration 0 to 20×10^{-6} molar and oxygen pressure 0.2 to 1.0 atm.

Experimental Results

The type of absorption curve is shown in Fig. 1. In all cases, except at $CuSO_4$ = 0 molar, the

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(1) M. B. Young and H. A. Young, THIS JOURNAL, 64, 2282 (1942).

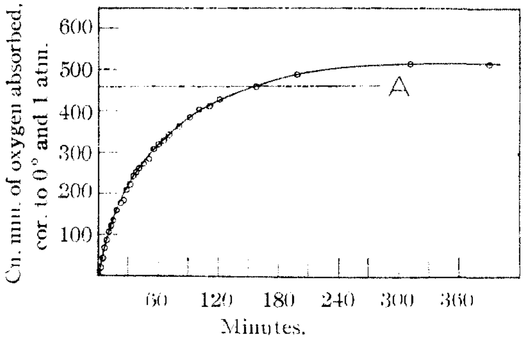

Fig. 1.—Absorption of oxygen at 37° and 1 atm. pressure by glutathione in alkaline solution: $GS^- = 0.00411$ *M*; $Cu^{++} = 10.14 \times 10^{-6}$ *M*; $OH^- = 0.1384$ *M*.

maximum slope occurs at zero time. The autocatalysis which is so characteristic of similar experiments at *p*H 11[1] is now missing. Line A represents the theoretical volume of oxygen required to convert the glutathione to the salt of the sulfinic acid. Actually, the oxygen absorbed is somewhat high (12% in Fig. 1) and occasionally a very slow continued absorption of oxygen is observed. Unlike experiments at *p*H 11, the excess oxygen absorption cannot be explained by the presence of hydrogen peroxide as a final product. Colorimetric tests with titanium sulfate show that (within the limits of the measurements) hydrogen peroxide is not present at the end of the experiments but that it is formed earlier in small amounts provided the copper sulfate concentration is sufficiently high. The fact that the temporary accumulation of hydrogen peroxide in experiments at *p*H 13 is not accompanied by an autocatalytic type of reaction is further confirmation to the conclusion drawn earlier[1] that hydrogen peroxide is not a catalyst for the reactions involved. In general, the trend of the experimental results has been toward the following qualitative correlation: The lower the concentration of copper sulfate catalyst, the less the accumulation of hydrogen peroxide (which remains as a final product at *p*H 11 and disappears at *p*H 13) and the nearer the final oxygen absorption approaches the theoretical value (G_2S_2 at *p*H 9–11; GSO_2^- at *p*H 13). The excess oxygen absorption in a series of experiments at *p*H 13 is shown in Column 5 of Table I. In column 6 is the concentration of the hydrogen peroxide produced at the times specified. Hydrogen peroxide at concentrations less than 1×10^{-6} molar could not be determined by the colorimetric method used. The production of some sulfonic acid probably accounts for the excess oxygen absorption at *p*H 13. However, even though the products were not isolated and identified, it is felt that the data of Table I as a whole indicate that the main reaction involved is one producing sulfinate ion.

TABLE I

COMPARISON BETWEEN EXCESS OXYGEN ABSORPTION AND HYDROGEN PEROXIDE PRODUCTION

GS^-	OH^-	$Cu^{++} \times 10^6$	O_2, atm.	Excess O_2 absorption, %	H_2O_2 produced, moles per liter
0.00433	0.1822	...	1	−2	
.00433	.1822	...	1	−1	
.00433	.1822	...	1	−2	
.00110	.1854	...	1	2	
.00110	.1854	...	1	3	
.00110	.1854	...	1	3	
.00226	.1918	...	1	−1	
.00226	.1918	...	0.5	1	
.00215	.0950	...	1	2	
.00215	.0950	...	0.5	0	
.00440	.169	3.73	1	10	
.00440	.169	7.45	1	6.5	
.00440	.169	15.5	1	9	
.00109	.171	3.7	1	13	
.00218	.172	3.7	1	6.5	
.00218	.166	15.5	1	9.0	
.00104	.1492	20.28	1	14	$<1 \times 10^{-5}$ at end of expt.
.00104	.1492	20.28	0.5	14	$<1 \times 10^{-6}$ at end
.00104	.1492	20.28	0.2	7.2	$<1 \times 10^{-6}$ at end
.00105	.1492	5.07	1	...	$<1 \times 10^{-5}$ at 90% completion
.00105	.1492	5.07	0.5	...	$<1 \times 10^{-5}$ at 90%
.00105	.1492	5.07	0.2	...	$<1 \times 10^{-6}$ at 90%
.00413	.1383	20.28	1	...	1×10^{-4} at 25%
.00104	.1492	15.21	1	8	......
.00208	.1455	15.21	1	...	1×10^{-5} at 50%
.00417	.1385	15.21	1	...	5×10^{-4} at 25%
.00104	.1492	None	1	...	$<1 \times 10^{-6}$ at 30%
.00411	.1384	20.28	1	...	5×10^{-4} at 30%
.00411	.1384	20.28	1	...	5×10^{-5} at 60%
.00411	.1384	20.28	1	...	5×10^{-6} at 85%
.00411	.1384	10.14	1	12	......
.00411	.1384	10.14	0.5	22	......
.00206	.0309	10.14	1	...	$<1 \times 10^{-5}$ near end
.00206	.0691	10.14	1	...	$<1 \times 10^{-5}$ near end
.00206	.1455	10.14	1	..	$<1 \times 10^{-5}$ near end

In the experiments in which no copper sulfate is added an induction period appears as is shown in Fig. 2.[2] The maximum rate occurs when the reaction is about 30% complete; thereafter, the type of reaction is similar to that in which copper sulfate is present. Line A has the same meaning as in Fig. 1. The fact that the reaction occurs at all indicates the presence of catalytic impurities in the reagents since Meldrum and Dixon[3] have shown that pure glutathione will not react with oxygen (*p*H 7.6). Our own former experiments[1] had shown the necessity of repeatedly distilling the water and of using a special heavy

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[2] One of the earlier experiments performed. The source of the water used to dissolve the reagents had higher concentrations of catalytic impurity than did later ones.

[3] N. U. Meldrum and M. Dixon, *Biochemical J.*, **24**, 1 (1930).

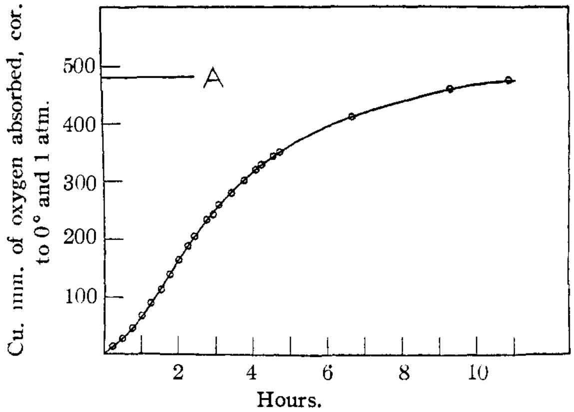

Fig. 2.—Absorption of oxygen by glutathione: $GS^- = 0.00433\ M$; $Cu^{++} = 0.00\ M$; $OH^- = 0.1822\ M$; $O_2 = 1$ atm.

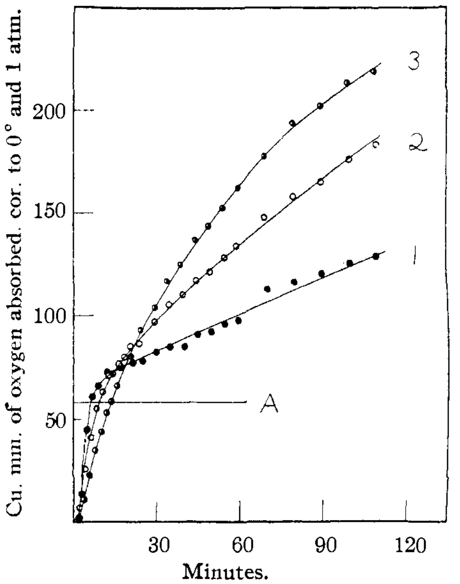

Fig. 3.—Absorption of oxygen by glutathione: $GS^- = 0.00206\ M$; $Cu^{++} = 10.14 \times 10^{-6}\ M$; $O_2 = 1$ atm.; in 1, 2, 3, $OH^- = 0.0309, 0.0691, 0.1455\ M$, respectively.

metal free brand of sodium hydroxide (Mallinckrodt). Least variation occurred with different samples of glutathione so the latter was assumed to be fairly free of heavy metal. The last assumption is supported by the present experiments in which—at constant sodium hydroxide and copper sulfate concentrations—the rate of oxygen absorption as glutathione varies indicates a first order reaction with respect to glutathione. Since both the nature and concentrations of the catalytic impurities are unknown in these so-called $Cu^{++} = 0$ experiments, they have been disregarded in the sections that follow.

Effect of Hydroxide Ion Concentration.—For the concentrations of glutathione considered (0.0010 to 0.0044 *M*), a hydroxide ion concentration of 0.1 *M* is sufficiently high to produce the continuous absorption curve shown in Fig. 1. Below that concentration a distinct break always occurs in the absorption rate corresponding—closely—to the conversion of the glutathione to the disulfide (see Fig. 3). Line A represents the theoretical volume of oxygen required to oxidize the mercaptan to the disulfide. The fact that the discontinuities occur slightly above the theoretical value at A is accounted for by the production of H_2O_2 as discussed in paper I. Apparently a primary reaction producing R_2S_2 is followed by one producing a higher oxidation product. As the *p*H decreases from 13 to 11, the follow reaction decreases rapidly in rate while the primary one remains essentially constant (or even increases) but in all cases the point of discontinuity in the curves representing the two oxidations is at a constant ordinate position—a position indicating disulfide production. It seems therefore that even at a *p*H of 13 where the curve becomes continuous, the initial reaction may primarily involve the oxidation from GS^- to G_2S_2. It is because of this assumption plus the fact that the rate law as derived from initial rates is the same (with respect to $CuSO_4$ and GS^- concentrations and to O_2 pressure) at a *p*H just under 13 where the discontinuity still exists as it is at *p*H 13 that it is felt justifiable, as is done later, to apply a rate law obtained at *p*H 13 to data obtained at *p*H 11. An increase in hydroxide ion concentration from 0.1 to 0.2 *M* produces only a very slight decrease in the initial reaction rates. Hence for the *p*H region 13–13.3 the reaction is considered to be independent of hydroxide ion.

Effect of Oxygen Pressure.—The reaction is essentially independent of oxygen pressure. In no experiment was there any change in rate of oxygen absorption as the oxygen pressure was reduced from 1 to 0.5 atm. Often with oxygen = 0.2 atm. a slight decrease in rate was noted as the reaction proceeded but the initial maximum rate usually agreed with those obtained at the higher pressures. Three experiments in which Cu^{++} and GS^- concentrations are constant and oxygen pressure = 1, 0.5, and 0.2 atm. are shown in Fig. 4. The fact that the total oxygen absorption at the lowest pressure is less than that at the higher ones is without significance. Variation was always found toward the end of the experiments and any one of them might show the highest total absorption. Line A represents the theoretical volume of oxygen required to convert the glutathione to the sulfinic acid.

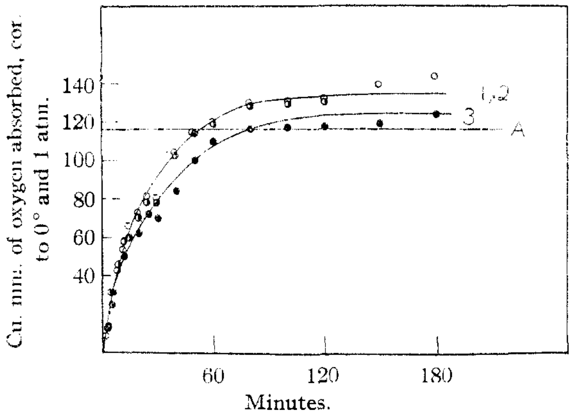

Fig. 4.—Absorption of oxygen by glutathione: GS$^-$ = 0.00104 *M*; Cu^{++} = 20.28 × 10^{-6} *M*; OH$^-$ = 0.1492 *M*; in 1 (○), 2 (◑), and 3, O_2 = 1, 0.5, 0.2 atm., respectively.

Effect of GS$^-$ and Cu^{++} Concentration.—A comparison of initial maximum slopes indicates that the reaction is first order with respect to GS$^-$ as is shown in Fig. 5. The circled point in curve 4 represents an initial slope in which a slight induction period makes its first appearance. In this case, as well as for all those in curve 5, the induction period has been disregarded and the initial slope extrapolated. Hence

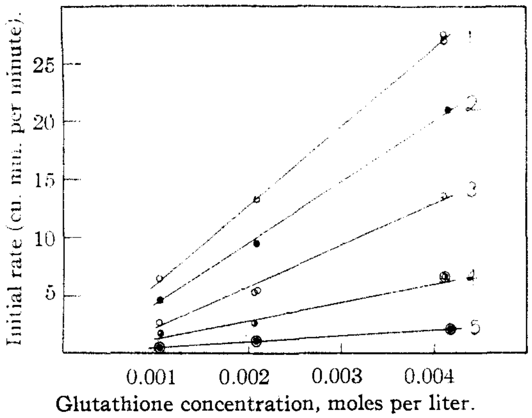

Fig. 5.—Variation of initial slope with glutathione concentration: in 1, 2, 3, 4, 5 Cu^{++} (10^6) = 20.28, 15.21, 10.14, 5.07, 0.00 *M*, respectively.

$$-\,dO_2/dt = k_a(GS^-)$$

A comparison of the values of k_a as determined by initial rates at various Cu^{++} concentrations is given in Table II and a plot of k_a against Cu^{++} is shown in Fig. 6. Except for very low concentrations of Cu^{++} a reasonably good straight line can be drawn which intercepts the origin. Hence

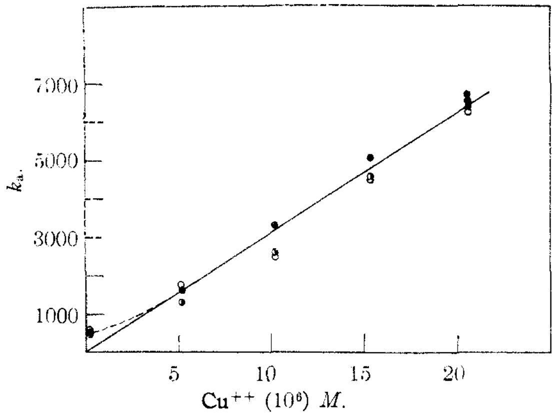

Fig. 6.—Variation of k_a with Cu^{++} concentration.

$$k_a = k(Cu^{++})$$

and

$$-\,dO_2/dt = k(Cu^{++})(GS^-)$$

The numerical value of k as determined by the slope of the line in Fig. 6 is

$$318 \times 10^6 \frac{\text{mm.}^3\ \text{min.}^{-1}}{(\text{moles/liter})^2}$$

TABLE II

VARIATION OF INITIAL RATE WITH GS$^-$ AND WITH Cu^{++}

No.	GS$^-$	OH$^-$	Cu^{++} × 10^6	Initial rate, cu. mm./minute	$\frac{\text{Initial rate}}{(GS^-)} = k_a$
1	0.00104	0.1492	0.00	0.60	577
2	.00105	.1492	5.07	1.83	1740
3	.00104	.1492	10.14	2.67	2570
4	.00104	.1492	15.21	4.65	4470
5	.00104	.1492	20.28	6.50	6240
6	.00208	.1455	0.00	1.03	495
7	.00206	.1456	5.07	2.78	1350
8	.00209	.1455	10.14	5.45	2610
9	.00206	.1455	10.14	5.37	2610
10	.00208	.1455	15.21	9.5	4570
11	.00209	.1455	20.28	13.3	6370
12	.00417	.1382	0.00	2.11	506
13	.00411	.1384	5.07	6.70	1630
14	.00411	.1384	10.14	13.7	3330
15	.00415	.1382	15.21	21.0	5060
16	.00413	.1383	20.28	27.0	6540
17	.00411	.1384	20.28	27.6	6710

k = 318 mm.^{3} min.$^{-1}$/(moles/liter)^2

For any one experiment, a plot of log GS$^-$ (assuming GSO_2 production) against time indicates a reaction which is first order with respect to GS$^-$ during the greater part of the reaction but one which becomes too rapid toward the end. Also if Cu^{++} = 0 the reaction is too slow at the beginning, corresponding to the induction period observed in these experiments.

The experiments presented in Table II were done in triplicate with O_2 = 1, 0.5 and 0.2 atm. Since the experimental points obtained at O_2 = 1 atm. were indistinguishable from those at O_2 = 0.5 atm., a single curve was drawn and one initial slope determined as representative of both. A separate curve was drawn with the data at O_2 = 0.2 atm. In a few cases the initial slopes were appreciably less than those obtained at the higher oxygen pressures. In experiments 2, 3, 11 and 13 the initial maximum slopes are 1.68, 2.00, 11.1 and 6.33 cu. mm. per minute, respectively, as compared with 1.83, 2.67, 13.1 and 6.70 at higher pressures.

Rate Law and Mechanism

In a former publication,[1] the auto-catalytic nature of certain reactions between glutathione and oxygen at *p*H 11 was attributed to the formation of a catalyst, assumed to be a peroxy radical of type GSO_2, the steady state of which often was not reached until the reaction was almost complete. The rate of production of this catalyst was dependent upon Cu^{++} and GS^-; the rate of continuation, upon a reaction with O_2; and the rate of destruction, upon a reaction with GS^-. Thus

$$\mathrm{Cu^{++} + GS^-} \xrightarrow{(\mathrm{O_2})} \mathrm{X} \qquad \text{(a)}$$

$$\mathrm{X + O_2} \xrightarrow{(\mathrm{GS^-})} \text{product} + \mathrm{X} \qquad \text{(b)}$$

$$\mathrm{X + GS^-} \xrightarrow{(\mathrm{O_2})} \text{product with destruction of X} \qquad \text{(c)}$$

Parentheses indicate that the substances are used in the reaction but do not enter into the rate law. When the maximum rates occurred near the end of the experiments where GS^- was reduced greatly in concentration, the total absorption of oxygen was assumed to be due mainly to reaction (b) and

$$\begin{aligned} -\mathrm{dO_2}/\mathrm{d}t &= k_\mathrm{b}(\mathrm{X})(\mathrm{O_2}) \\ &= k_\mathrm{b}\frac{k_\mathrm{a}}{k_\mathrm{c}}(\mathrm{Cu^{++}})(\mathrm{O_2}) \qquad \text{(d)} \end{aligned}$$

Conversely, if the rate of reaction (c) is large with respect to that of (b), a reaction independent of O_2 and first order with respect to GS^- and to Cu^{++} results. The results obtained in the present series of experiments where hydroxide ion is relatively high seem to place the reactions in this later category.

A possible series of reactions could be

$$\mathrm{Cu(OH)_2} + n(\mathrm{GS^-}) \overset{k_1}{=} \mathrm{Cu^{++}(GS^-)}_n\text{·rapid, complete} \qquad (1)$$

$$\mathrm{Cu^{++}(GS^-)}_n + \mathrm{GS^-} \xrightarrow{k_2} \mathrm{Cu^{+}(GS^-)}_n + \mathrm{GS} \qquad (2)$$

$$\mathrm{Cu^{+}(GS^-)}_n + \mathrm{O_2} \xrightarrow{k_3} \mathrm{Cu^{++}(GS^-)}_n + \mathrm{O_2^-} \qquad (3)$$

$$\mathrm{O_2^- + GS^- + 2H_2O} \overset{k_4}{=} \mathrm{GS + H_2O_2 + 2\ OH^-} \qquad (4)$$

$$\mathrm{GS + O_2} \overset{k_5}{=} \mathrm{GSO_2} \qquad (5)$$

$$\mathrm{GSO_2 + O_2} \xrightarrow{k_6} \mathrm{GSO_4} \qquad (6)$$

$$\mathrm{GSO_4 + GS^-} \xrightarrow{k_7} \mathrm{GSO_2^- + GSO_2} \qquad (7)$$

$$\mathrm{GSO_2 + GS^-} \xrightarrow{k_8} \mathrm{GSO_2.GS^-} \qquad (8)$$

$$\mathrm{GSO_2.GS^- + GSO_4 + 2\ OH^-} \xrightarrow{k_9} \mathrm{3\ GSO_2^- + H_2O_2} \qquad (9)\ \text{etc.}$$

Since the copper concentration is small compared to the GS^-, the complex formation in (1) does not appreciably affect the GS^- concentration.

Representing the complex ion concentration by (Cu^{++})

$$\begin{aligned} -\mathrm{dO_2}/\mathrm{d}t &= k_3(\mathrm{Cu^{++}})(\mathrm{O_2}) + k_5\,(\mathrm{GS})(\mathrm{O_2}) + k_6(\mathrm{GSO_2})(\mathrm{O_2}) \\ &= k_2(\mathrm{Cu^{++}})(\mathrm{GS^-}) + 2k_2\,(\mathrm{Cu^{++}})(\mathrm{GS^-}) + (k_2k_6/k_8)(\mathrm{Cu^{++}})(\mathrm{O_2}) \\ &= 3k_2(\mathrm{Cu^{++}})(\mathrm{GS^-}) + (k_2k_6/k_8)(\mathrm{Cu^{++}})(\mathrm{O_2}) \qquad (10) \end{aligned}$$

If k_8 is large compared to the product of k_2 and k_6 so that term 2 is negligible

$$-\mathrm{dO_2}/\mathrm{d}t = 3k_2(\mathrm{Cu^{++}})(\mathrm{GS^-})$$

and $k_2 = (318/3) \times 10^6$

$$= 106 \times 10^6\ \mathrm{mm.^3\ min.^{-1}/(moles/liter)^2}$$

An alternative reaction for (2) is

$$\mathrm{Cu^{++}(GS^-)}_n + \mathrm{GS^-} \rightleftarrows \mathrm{Cu^{++}(GS^-)}_n\mathrm{GS^-} \qquad (2^1)$$

followed by

$$\mathrm{Cu^{++}(GS^-)}_n\mathrm{GS^-} \longrightarrow \mathrm{Cu^{+}(GS^-)}_n + \mathrm{GS}$$

If equations 1–10 are applicable throughout the *p*H range 11–13.3 (a plausible assumption since the constancy of the position of the discontinuities in the curves of Fig. 3 indicates that the early steps of the reaction at *p*H 13 may be similar to those at *p*H 11) we may write equation (10) as

$$-\mathrm{dO_2}/\mathrm{d}t = c_1(\mathrm{Cu^{++}})(\mathrm{GS^-}) + c_2(\mathrm{Cu^{++}})(\mathrm{O_2}) \qquad (11)$$

and assign to $c_2 = k_2k_6/k_8$ the value previously determined at *p*H 11 and 1 atm. pressure, namely

$$11.2 \times 10^5\ \mathrm{mm.^3\ min.^{-1}/(moles/liter)(atm.)}$$

If k_8 is a function of hydroxide ion between *p*H 11 and *p*H 13 while c_1 is independent of hydroxide ion, the contribution of term 2 to the oxygen absorption will decrease with increase in *p*H and eventually become negligible. For example, at *p*H 11 with initial GS^- = 0.0022 molar, O_2 = 1 atm., and $Cu^{++} = 1 \times 10^{-5}$ molar, the maximum

TABLE III

COMPARISON BETWEEN OBSERVED AND CALCULATED MAXIMUM SLOPES

$Cu^{++} \times 10^6$	GS^- (initial)	O_2, atm.	% completion at maximum rate (±5%)	Observed maximum	Calcd. maximum	% Contribution of term 1
10.08	0.00220	1	85	11.4	12.3	8
10.08	.00220	0.5	80	7.60	7.0	20
10.08	.00220	0.2	71	4.42	4.3	47
7.56	.00217	1	64	8.50	10.3	18
7.56	.00217	0.5	60	5.85	6.3	33
7.56	.00217	0.2	67	3.32	3.4	51
5.04	.00220	1	67	5.75	6.8	17
5.04	.00220	0.5	64	4.00	4.1	31
5.04	.00220	0.2	67	1.89	2.3	51
2.52	.00220	1	70	2.55	3.4	16
2.52	.00220	0.5	62	1.47	2.1	32
2.52	.00220	0.2	68	0.72	1.1	50
1.26	.00220	1	55	.93	1.8	22
1.26	.00220	0.5	58	.76	1.1	35
1.26	.00220	0.2	55	.50	0.68	58
0.504	.00220	1	40	.58	.77	28
.504	.00220	0.5	0	.51	.63	56
.504	.00220	0.2	0	.50	.47	76
0	.00222	1	0	.50	0	
0	.00222	0.5	0	.50	0	
0	.00222	0.2	0	.50	0	

rate occurs when the reaction is about 90% complete. Hence

$$(-\,dO_2/dt)_{max.} = (Cu^{++})[(31.8 \times 10^7)(0.00022) + 11.2 \times 10^5]$$
$$= 0.7 + 11.2 = 11.9$$

and term 2 dominates, being 16 times as large as term 1. At *p*H 13, the maximum rate occurs initially and

$$(-\,dO_2/dt)_{max.} = (Cu^{++})[(31.8 \times 10^7)(0.0022) + (11.2 \times 10^5/100)]$$
$$= 7.0 + 0.1 = 7.1$$

and term 1 is 60 times as large as term 2. Further increase in *p*H does not change the value of $(-dO_2/dt)_{max.}$ appreciably. The experimental slopes obtained for the above are 11.4 and 6.8, respectively. (The latter value is interpolated for $GS^- = 0.0022$ from the curve of Fig. 6.) The agreement is fairly good. Also, as previously stated, increase of *p*H from 13 to 13.3 does not affect the rate.

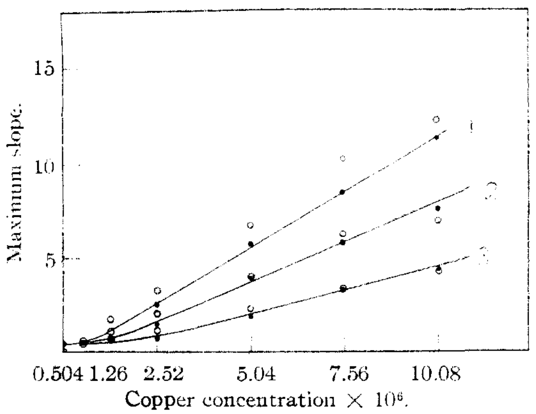

Fig. 7.—Comparison between observed (●) and calculated (○) maximum slopes at *p*H 11. O_2 pressures in 1, 2, 3 are 1, 0.5, 0.2 (air) atm., respectively.

In the first five columns of Table III are experimental data obtained at *p*H 11. In column 5 are the observed maximum slopes occurring at the positions indicated in column 4. These maxima are plotted as filled points in Fig. 7 (Fig. 8 of the former publication[1]). In column 6 are the same maxima as calculated by equation (11). Column 7 represents the contribution in % to $(-dO_2/dt)_{max.}$ of term 1 in equation (11). Considering the error in determining the position of the maxima and the uncertainty of the value of C_2, the agreement between observed and calculated maxima is generally fair enough to warrant confidence in the use of the equation. More particularly, the trends are in agreement. The approach to disappearance of oxygen dependency at low Cu^{++} concentrations—especially at lower oxygen pressures—associated with changes in the shape of the curve can be explained by an equation of the type presented. The positive initial rate at zero Cu^{++} concentration is assumed to be caused by impurities in the reagents.

It is to be noted that oxygen appears to the first power in the second term of the rate expression (11). Formerly[1] this term was expressed as $k(Cu^{++})(O_2)^{1/2}$. While it is true that the autocatalytic reactions at *p*H 11 in which the maximum rates occurred near the end of the experiments indicated a half order with respect to oxygen, it is now felt that this apparent agreement with the half power law is fortuitous and that equation (11) with its more general applicability is preferable.

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Summary

1. The rate of absorption of oxygen by glutathione in the *p*H range 13 to 13.3 and in the presence of copper sulfate catalyst has been measured. The effects of changes in copper sulfate and glutathione concentrations and oxygen pressure are presented.

2. The rate law is given and a mechanism proposed.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE OHIO STATE UNIVERSITY]

Addition Compounds of Sulfur Dioxide[1]

BY NOEL F. ALBERTSON AND W. CONARD FERNELIUS[2]

Sulfur dioxide forms numerous addition compounds with organic substances. While almost all of these compounds are formed with nitrogen bases,[3] a few are formed with oxygen-containing substances: ether,[4] camphor,[5] methanol,[6] acetone,[7] and trimethylamine oxide.[3,8]

In the first three cases, the existence of these addition compounds has been established by thermal analyses.

The main object of the present investigation was the determination of the temperature–composition diagrams of several systems comprising sulfur dioxide and some simple oxygen-containing compound. In this way some idea of the generality of the formation of addition compounds of sulfur dioxide with oxygen compounds could be established.

Experimental

Preparation of Materials.—Sulfur dioxide was distilled from a small commercial cylinder directly into a storage ampoule after drying over barium oxide and phosphorus pentoxide. The observed melting point was −74.9°.

Acetone was purified by refluxing for three and one-half hours with potassium permanganate and potassium hydroxide. It was then distilled through a long fractionating column and a small middle fraction was taken. The observed melting point was −94.1° as compared to literature values[9] of −93.9° to −94.6°.[10]

Dioxane was refluxed with sodium hydroxide and distilled from sodium. It was then treated with a small amount of fuming sulfuric acid and fractionated. Additional refluxing with sodium and distillation from sodium gave a product melting at 11.6°. The literature values have been summarized by Hess and Frahm.[11] They report a melting point of 11.80 ± 0.01°.

Other compounds were purified by distillation. A boiling point of 75° at 53 mm. was observed for anisole.

Apparatus.—The apparatus was essentially the same as that described by Booth and Martin.[12]

The System Sulfur Dioxide–Ethylene Oxide

The formation of an addition compound between sulfur dioxide and dimethyl ether is best explained by assuming that the ether oxygen atom shares a pair of its electrons to form a covalent bond with the sulfur dioxide molecule.[13] It seemed very likely that ethylene oxide should also form an addition compound.

The results of the thermal analyses are shown in Fig. 1. The maximum due to the 1:1 addition compound is at −95°. Eutectics occur at 33 and 91 mole per cent. ethylene oxide at −115.5° and −114.2°, respectively. Solutions containing 0.556 and 0.559 mole fraction of

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[1] From a dissertation presented by Noel F. Albertson (1941) for the Degree of Doctor of Philosophy. Presented before the Division of Physical and Inorganic Chemistry at the Buffalo meeting of the American Chemical Society, September, 1942.

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[3] (a) For examples see J. R. Bright and W. C. Fernelius, THIS JOURNAL, **65**, 637–9 (1943). (b) For compounds of SO_2 with $(CH_3)_3N$ and $(CH_3)_3NO$ see A. B. Burg, *ibid.*, **65**, 1629 (1943).

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[6] G. Baumé and G. Pamfil, *Compt. rend.*, **152**, 1905 (1914); *J. chim. phys.*, **12**, 256–269 (1914).

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[12] H. S. Booth and D. R. Martin, THIS JOURNAL, **64**, 2198–2205 (1942).

[13] The possible structure of sulfur dioxide addition compounds has been discussed by J. R. Bright and J. J. Jasper, *ibid.*, **63**, 3487 (1941).