TABLE IV

THERMODYNAMIC CONSTANTS FOR THE FIRST IONIZATION OF CARBONIC ACID

t	C	Λ_c	Λ_e	f^2	$K_1 \times 10^7$	pK_1 Obsd.	pK_1 Computed	ΔH, cal.
0°	0.03284	0.7040	247.2	0.9785	2.613	6.5830	6.5839	4484
15°	.03282	1.1410	335.4	.9764	3.722	6.4293	6.4300	2952
25°	.03275	1.4401	392.6	.9746	4.310	6.3655	6.3654	2075
38°	.03262	1.8040	464.0	.9731	4.817	7.3173	6.3173	1109

that ΔH assumes a value of zero at 58.1°. Consequently, pK_1 would be expected to pass through a minimum (6.293) and K_1 to reach a maximum (5.09×10^{-7}) at that temperature. Such behavior is in accord with similar results on all other weak acids, so far as they have been studied.[14]

In the last column of Table IV are listed values for ΔH in calories, computed from equation (11′). The value at 25° ($\Delta H = 2075$ calories) is in excellent agreement with that derived from e. m. f. measurements at 18 and 38° by Stadie and Hawes,[15] and also by Cullen, Keeler and Robinson,[16] both giving $\Delta H = 2050$ calories. Direct calorimetric measurements by Thomsen[17] at room temperature, probably 15–16°, gave 2800 calories in reasonable agreement with our value of 2952 at 15°.

Summary

New measurements have been made at 25° on the conductances of solutions of carbonic acid and of potassium bicarbonate. The relative conductances at 0, 15, 25 and 38° of saturated carbonic acid solution and of potassium bicarbonate, potassium chloride and hydrochloric acid at 0.001 normal have also been determined. From these data the thermodynamic dissociation constant of carbonic acid as a monobasic acid has been obtained for the temperatures given. These values have been used in obtaining equations by means of which the ionization constant K_1 and the heat ΔH of the reaction $H_2O + CO_2 = H^+ + HCO_3^-$ are expressed as functions of the temperature. The values of the constant K_1 are 4.31×10^{-7} at 25° and 4.82×10^{-7} at 38°, in reasonable agreement with the corresponding values 4.5×10^{-7} and 4.9×10^{-7} obtained by MacInnes and Belcher at these temperatures.

NEW YORK, N. Y. RECEIVED JUNE 6, 1935

(14) Harned and Embree, THIS JOURNAL, **56**, 1050 (1934).

(15) Stadie and Hawes, *J. Biol. Chem.*, **77**, 241 (1928).

(16) Cullen, Keeler and Robinson, *ibid.*, **66**, 301 (1925).

(17) Thomsen, "Thermochemische Untersuchungen," Leipzig, 1882.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF HARVARD UNIVERSITY]

The Photolysis of Dry Ozone at λλ 208, 254, 280 and 313 mμ. II. Reaction Kinetics

BY LAWRENCE JOSEPH HEIDT

Recent data from this Laboratory[1] on the photolysis of dry ozone, largely at λ 208 mμ, gave quantum yields, ϕ, referred to ozone as large as 6.7. This strongly suggested a chain mechanism; but the decrease in ϕ with p_{O_3}/p_{O_2} was not so great as that given by Beretta and Schumacher[2] at λ 313 mμ, nor was ϕ independent of the light intensity. Further interpretation of the data was therefore postponed until a check was made upon the work at λ 313 mμ and until the influences of concentrations and wave length upon quantum yields were more fully established. Such data are presented here.

The experimental procedure, precautions, and corrections were the same as previously followed.[1] At λ 313 mμ an inverted U type quartz mercury arc lamp[3] was used as a light source. The trap at the top of the inverted U was omitted. Instead, the U was tilted so that the plane containing it made an angle of approximately 15° with the plane containing the plungers. The plunger connected to the upper positive electrode was seated; the other was slightly unseated. The luminous column was contained in a quartz tube 4 mm. inside diameter and 7 mm. o. d. The arc length was 60 mm. The lamp was operated on a 110–v. storage battery source at from 2 to 4 amp. It was as intense, constant and durable for slit illumination as its higher voltage type predecessor.[3]

(1) Heidt and Forbes, THIS JOURNAL, **56**, 2365 (1934).

(2) Beretta and Schumacher, *Z. physik. Chem.*, **17B**, 417 (1932).

(3) Forbes and Heidt, THIS JOURNAL, **53**, 4349 (1931).

The actinometer solution at λ 313 mμ was 0.003 *M* in uranyl oxalate and 0.003 *M* in oxalic acid. Its quantum yield was taken as 0.57.[4] The remainders of the solutions and apparatus were the same as those employed at λλ 208, 254 and 280 mμ.[1] More than 97%, by actual measurement,[5] consisted of light within 5 mμ of the desired wave length.

Partial pressures of ozone, p_{O_3}, and oxygen, p_{O_2}, at total pressure, $P = p_{O_3} + p_{O_2}$, were calculated from the observed difference between P and total end pressure, P_f. To obtain P_f, the reaction cell was irradiated with light from an Hanovia mercury arc lamp of quartz placed 2 cm. from the front window of the cell until P became constant over eighteen hours. This was followed by flaming to a dull red heat, the cell, capillary connections and the quartz spiral pressure gage. The system was then allowed to cool to room temperature, whereupon P_f was again determined. The difference between P_f as determined by irradiation and by flaming never exceeded 1 mm. The volume of the system was 42 cc. The dead space outside the quartz reaction cell was 2.0 cc; the part at room temperature was 1.3 cc.

The results are tabulated in Tables I and II. The subscripts appended to the serial numbers give the number of experiments in the group if greater than one. Pressures were recalculated to 0° in mm. of mercury at 0°. A barred quantity denotes an average. Quantum yields, ϕ, were referred to the number of ozone molecules decomposed (calculated from $2\Delta P$) per quantum absorbed. In representative cases, the subtracted quantities under ΔP are the corrections for the dark rate. For comparison, corresponding values of ϕ given by B. and S.[2] are also included. At λλ 208, 254 and 280 mμ, absorption of light by ozone was taken as complete.[6] At λ 313 mμ, ϕ is given for the value of the extinction coefficient, $k = \log I_0/I/p_{O_3}d$ (p_{O_3} in mm. and d in cm.), used by B. and S.,[2] namely, 0.00092.[6b]

Table II, Series 6, groups 1 and 2, and groups 9, 10 and 11 show corresponding values of ϕ to be approximately equal at λλ 208 and 313 mμ. The earlier work[1] also showed ϕ to be approximately equal at λλ 208, 254 and 280 mμ and frequently to exceed 4.

The average ten-degree temperature coefficient for the photolysis given in Series 6, at λ 313 mμ, is $\delta_{10^\circ}\phi = 1.15$ over the range 0 to 60°. It is apparently independent of the mole fraction of ozone and of the temperature interval after ϕ was corrected for the dark reaction between pressure readings before and after photolysis. There was no observable after-effect. Earlier work[1] gave $\delta_{10^\circ}\phi = 1.18$ over the range -80 to 0°. B. and S. give $\delta_{10^\circ}\phi = 1.25$ over the range 0 to 35°.

The dark rates in Series 6 for which $P_f = 584$ mm. were as follows. At 23 ± 2° they were $1.46/1080 = 1.3 \times 10^{-3}$ mm./min. at $\bar{P} = 446$ and $\bar{p}_{O_3} = 276$ and $0.7/1300 = 0.6 \times 10^{-3}$ at $\bar{P} = 497$.

At 40 ± 1° they were $1.2/37 = 33 \times 10^{-3}$ at $\bar{P} = 470$; $2.4/310 = 8 \times 10^{-3}$ at $\bar{P} = 480$ and $1.7/980 = 1.7 \times 10^{-3}$ at $\bar{P} = 525$.

At 60 ± 1° they were $2.0/105 = 19 \times 10^{-3}$ at $\bar{P} = 530$; $0.8/50 = 16 \times 10^{-3}$ at $\bar{P} = 540$; $0.7/115 = 6 \times 10^{-3}$ at $\bar{P} = 555$ and $4.3/940 = 4.5 \times 10^{-3}$ at $\bar{P} = 559$.

These give a *ten-degree temperature coefficient for the dark rate* of 3 ± 0.1 between 20 and 60° for small mole fractions of ozone in oxygen. At corresponding mole fractions Glissmann and Schumacher[7] give 3 ± 0.1 between 70 and 110°.

Figure 1 shows plots of $1/\phi$ against $p_{O_2} \times (p_{O_2} + p_{O_3})/p_{O_3}$. Circles represent the data of B. and S.[2] at 7.5 ± 3°, λ = 313 mμ, and filled circles Series 3 of the previous work from this Laboratory[1] at λ 208 mμ. Singly flagged circles represent the data of Table I, doubly flagged circles, Table II at λ 313 mμ and bisected circles, Table II at λλ 208 and 254 mμ; all at 22 ± 3°. Although the initial partial pressure of pure dry ozone varied from 177 to 390 mm., the data of Tables I and II even at λ 313 mμ, are in good agreement with the earlier work of this Laboratory. Plotted on a more condensed scale, they are also in good agreement with the average of the data of Warburg[8] at λ 254 mμ represented by the flagged filled circle. They agree with those of B. and S. only if ϕ is reduced by one-half. Possibly the latter referred their ϕ to the increase in the number of molecules in the reacting system per quantum absorbed; the number of ozone molecules decomposed is twice this number. Or they

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(4) Forbes and Heidt, THIS JOURNAL, **56**, 2363 (1934).

(5) Method of Heidt and Daniels, *ibid.*, **54**, 2384 (1932).

(6) (a) Meyer, *Ann. Physik*, **12**, 849 (1903); (b) Fabry and Buisson, *Compt. rend.*, **156**, 782 (1913); (c) Ny and Choong, *Chinese J. Physics*, **1**, 38 (1933).

(7) Glissmann and Schumacher, *Z. physik. Chem.*, **21B**, 323 (1933).

(8) Warburg, *Sitzber. preuss. Akad. Wiss.*, 644 (1913).

TABLE I

Serial number	λ in mμ	$\bar{P}$	$\bar{p}_{O_3}$	$\bar{p}_{O_2}$	$\bar{p}_{O_2}\bar{P}/\bar{p}_{O_3}$	Cell temp., °C.	Quanta abs./min. $E_0 \times 10^{-16}$	Time of photolysis, min.	ΔP	ϕ	$1/\phi$
5- 1	208-4 Zn	179	174	5	*5*	19.8	11.1	12	2.70	6.2	*0.16*
2		181	168	13	*14*	20.5	8.6	10	1.40	5.0	*.20*
3		183	163	19	*21*	21.0	8.6	15	2.40	5.7	*.18*
4		186	160	26	*30*	21.3	7.8	13	2.05	6.2	*.16*
5		189	153	35	*43*	21.8	9.5	7	1.15	5.4	*.19*
6		190	151	39	*49*	22.1	9.5	9.3	1.25	4.3	*.23*
7		192	148	44	*57*	22.4	8.2	15	1.90	4.7	*.21*
8		195	142	53	*73*	21.0	7.4	19	2.55	5.6	*.18*
9		197	138	59	*84*	21.6	7.8	15	1.75	4.5	*.22*
10		206	119	87	*151*	23.0	8.3	19	2.10	4.1	*.24*
11		209	113	96	*178*	23.1	8.2	18	1.80	3.8	*.26*
12		211	109	102	*198*	23.3	8.0	19	1.95	3.8	*.26*
13		225	82	143	*392*	24.0	5.2	17	1.05	3.6	*.28*
14		226	79	147	*421*	23.4	7.5	23	1.80	3.2	*.31*
15		236	59	177	*710*	23.7	6.7	22	1.35	2.8	*.36*
16		238	56	182	*775*	20.7	8.0	21	1.20	2.1	*.48*
17		247	37	210	*1400*	21.0	7.6	25	0.85	1.4	*.72*
18		248	35	213	*1510*	21.9	7.0	24	0.70	1.4	*.72*
19		249	33	216	*1630*	22.2	6.0	24	0.80	1.8	*.56*
	P_f = 266						Average 7.8				

TABLE II

Serial number	λ in mμ	$\bar{P}$	$\bar{p}_{O_3}$	$\bar{p}_{O_2}$	$\bar{p}_{O_2}\bar{P}/\bar{p}_{O_3}$	Cell temp., °C.	Quanta abs./min. $E_0 \times 10^{-16}$	Time of photolysis, min.	ΔP	ϕ	ϕ given by B. and S.[2]	$\left(\frac{\phi_T}{\phi_{T'}}\right)^{10/(T-T')}$
6- 1a	*208-4 Zn*	421	325	96	125	22.5	12	23.5	3.35	*3.6*		
b		424	319	105	140	22.6	9.5	24.0	2.95	*4.0*		
2a	*313 Hg*	434	299	135	196	*20.9*	8.6	35.5	3.55	*3.5*	2.1	
b		437	293	144	215	*20.9*	4.1	57.5	2.50	*3.3*		
3a		444	279	165	262	*0.2*	11.2	31.5	2.70	*2.3*		
b		447	273	174	285	*.2*	6.6	41.8	2.10	*2.3*		*1.15*
4_2		449	269	180	300	*22.3*	6.7	39.8	2.20	2.9	2.0	
5_2		473	222	250	533	*22.7*	3.1	43.0	1.20	3.1	1.2	
6a		477	213	264	590	*40.0*	9.5	23.0	2.8–0.6	3.1		
b		481	205	276	650	*40.0*	8.4	25.0	2.7–0.3	3.5		*1.14*
7_2		488	191	297	762	*19.8*	9.2	29.0	1.90	2.1	1.1	
8_2		494	180	313	860	*0.1*	5.8	43.0	1.05	1.3		*1.18*
9_2		496	175	321	910	*21.4*	7.2	32.6	1.25	1.7	0.9	
10_2	*208-4 Zn*	500	166	335	1005	21.9	16.2	26.4	2.80	*2.0*		
11_3	*313 Hg*	517	133	384	1500	23.8	5.2	61.7	1.90	*1.9*		
12_3		522	123	399	1697	*23.2*	7.6	44.8	1.85	1.7		*1.14*
13_3		529	109	420	2050	*40.0*	4.5	101.0	2.60	2.1		*1.14*
14a		542	83	459	3000	*60.3*	8.2	50.0	4.5–0.7	2.9		
b		546	75	471	3440	*60.3*	7.4	46.5	4.6–1.4	2.8		
c		551	65	486	4120	*60.3*	7.7	79.0	5.4–0.8	2.3		
15_3		568	31	537	*9850*	*23.8*	3.1	85.2	1.10	1.3		*1.15*
16_2		570	27	543	11500	*60.2*	4.3	82.0	2.35	2.1		
17_2	*254-2 Zn*	581	5	576	*67000*	24.0	18.6	73.0	0.90	0.2		
	P_f = 584										Average	1.15

may have underestimated the amount of false light; they made use of filters to render their light monochromatic.

The decrease in ϕ with increase in the light intensity and/or extinction as it varied with wave length at λλ 208, 254 and 280 mμ,[1] does not alter the main trend of the increase in $1/\phi$ with $p_{O_2}P/p_{O_3}$. At λ 313 mμ neither B. and S. nor the author observed any dependence of ϕ upon light intensity.

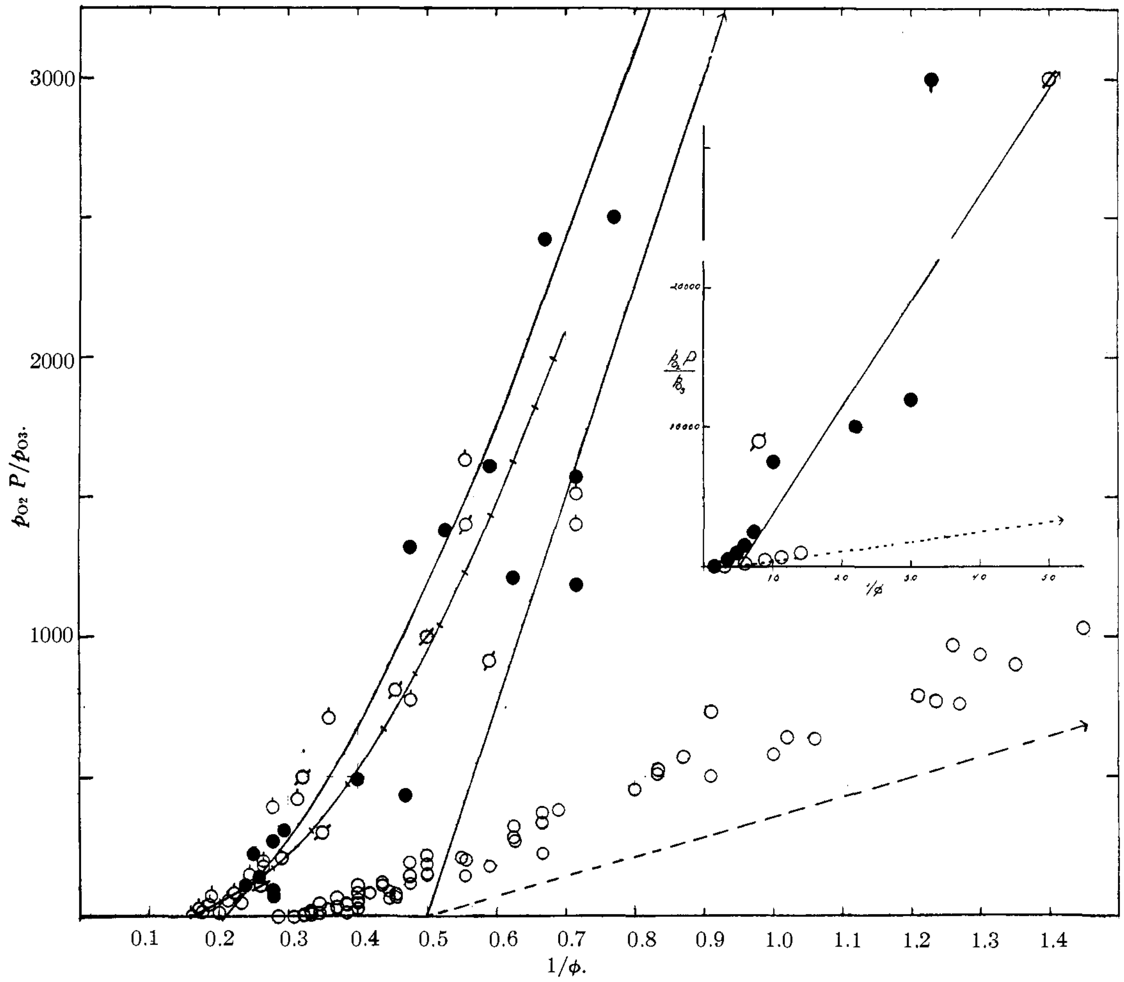

Fig. 1.—The curves are hypothetical. Circles represent the data of Beretta and Schumacher[2] at λ 313 mμ; the flagged filled circle on the sub-plot, the average of the data of Warburg[8] at λ 254 mμ; and the remaining symbols, the data from this Laboratory at λλ 208, 254, 280 and 313 mμ.

The curves are hypothetical. Within the limits of experimental error they agree with the observed increase in 1/φ with $p_{O_2}(p_{O_2} + p_{O_3})/p_{O_3}$. At large mole fractions of ozone where the experimental accuracy in 1/φ is best, the curves for Series 3 and 5 cross and follow the data very closely. They also approach asymptotically the straight lines drawn through the average of the data at small mole fractions of ozone.

Discussion

A reaction mechanism for the photochemical decomposition of ozone was postulated by Schumacher[9] in 1932, It was added to by Ritchie[10] in 1934. A summary of their hypotheses follows.

$$k_1 \quad O_3 + h\nu \longrightarrow O_2' + O$$
$$k_2 \quad O + O_3 \longrightarrow O_2' + O_2'$$
$$k_2S_2 \quad O + S \longrightarrow {}^1/_2O_2 + S$$
$$k_3 \quad O + O_2 + O_2 \longrightarrow O_3 + O_2$$
$$k_3' \quad O + O_2 + O_3 \longrightarrow O_3 + O_3$$
$$k_3S_3 \quad O + O_2 + S \longrightarrow O_3 + S$$
$$k_4 \quad O_2' + O_3 \longrightarrow O_2 + O_2 + O$$
$$k_5 \quad O_2' + O_3 \longrightarrow O_2 + O_3$$
$$k_5' \quad O_2' + O_2 \longrightarrow O_2 + O_2$$
$$k_5S_5 \quad O_2' + S \longrightarrow O_2 + S$$

To the left of the indicated reactions are given the corresponding rate constants. The reactions (k_3S_3) and (k_5S_5) involving the surface, S, have been added; and for absorption in the ultraviolet, O_2' in (k_1) has replaced O_2. The homogeneous recombination of oxygen atoms has been omitted because of their relatively small concentration in the presence of ozone and oxygen.

If $\alpha O_2'$ are produced in (k_1) and $\beta O_2'$ in (k_2), equations I, II and III follow

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(9) Schumacher, *Z. physik. Chem.*, **17B**, 405 (1932).

(10) Ritchie, *Proc. Roy. Soc.* (London), **A146**, 848 (1934).

$$\text{(I)}\qquad [\mathrm{O}] = I_{\text{abs.}}\left[\frac{\left(\dfrac{k_5[\mathrm{O_2}] + k_5'\,[\mathrm{O_3}] + k_5S_5}{k_4[\mathrm{O_3}]} + 1 + \alpha\right)}{\left(\dfrac{k_5[\mathrm{O_2}] + k_5'[\mathrm{O_3}] + k_5S_5}{k_4[\mathrm{O_3}]} + 1 - \beta\right)k_2[\mathrm{O_3}] + \left(\dfrac{k_5[\mathrm{O_2}] + k_5'[\mathrm{O_3}] + k_5S_5}{k_4[\mathrm{O_3}]} + 1\right)[\mathrm{O_2}](k_3[\mathrm{O_2}] + k_3'[\mathrm{O_3}] + k_3S_3) + k_2S_2}\right] = I_{\text{abs.}}\,B$$

$$\text{(II)}\qquad [\mathrm{O_2}'] = I_{\text{abs.}}\left[\frac{B\{k_2[\mathrm{O_3}] + k_2S_2 + [\mathrm{O_2}](k_3[\mathrm{O_2}] + k_3'[\mathrm{O_3}] + k_3S_3)\} - 1}{k_4[\mathrm{O_3}]}\right]$$

and, as $\phi = -\dfrac{\mathrm{d}[\mathrm{O_3}]}{\mathrm{d}t}\Big/I_{\text{abs.}}$, it follows that

$$\text{(III)}\qquad \frac{1}{\phi} = \underbrace{\frac{\left(\dfrac{k_5[\mathrm{O_2}] + k_5'[\mathrm{O_3}] + k_5S_5}{k_4[\mathrm{O_3}]} + 1 - \beta\right)}{\left(\dfrac{k_5[\mathrm{O_2}] + k_5'[\mathrm{O_3}] + k_5S_5}{k_4[\mathrm{O_3}]} + 1 + \alpha\right)(2 + S_2/[\mathrm{O_3}])}}_{\text{Term I}} + \underbrace{\frac{\left(\dfrac{k_5[\mathrm{O_2}] + k_5'[\mathrm{O_3}] + k_5S_5}{k_4[\mathrm{O_3}]}\right) + 1}{\left(\dfrac{k_5[\mathrm{O_2}] + k_5'[\mathrm{O_3}] + k_5S_5}{k_4[\mathrm{O_3}]} + 1 + \alpha\right)}\,\frac{1}{2}\left[\frac{[\mathrm{O_2}](k_3[\mathrm{O_2}] + k_3'[\mathrm{O_3}] + k_3S_3) + k_2S_2}{k_2[\mathrm{O_3}] + k_2S_2}\right]}_{\text{Term II}}$$

From III, $1/\phi$ is equal to the sum of two terms, the first of which increases to $1/(2 + S_2/(\mathrm{O_3}))$ or $^1/_2$ (very nearly) as $p_{\mathrm{O_2}}$ approaches $(p_{\mathrm{O_2}} + p_{\mathrm{O_3}})$, and the second of which increases to a constant $k_3/2k_2$ (very nearly) times $p_{\mathrm{O_2}}(p_{\mathrm{O_2}} + p_{\mathrm{O_3}})/p_{\mathrm{O_3}}$. The experimental work (see Fig. 1) shows a similar increase in $1/\phi$ with this ratio.[11] The constant, $k_3/2k_2$, is the reciprocal of the slope of the straight line (Fig. 1, solid line) which the data approach at small mole fractions of ozone. Its intercept on the $1/\phi$ axis equals the maximum value of the first term, *i. e.*, $^1/_2$ (very nearly), as $p_{\mathrm{O_2}} \longrightarrow (p_{\mathrm{O_2}} + p_{\mathrm{O_3}})$. From the data of this Laboratory at 22 ± 3° its slope is 7500 ± 800 mm./$1/\phi$ corresponding to 680 given by B. and S. at 7.5 ± 3°, Fig. 1 dotted line.

If the wall effect is negligible, $S_n = 0$. Then, when $p_{\mathrm{O_2}} = 0$, term II $= 0$ and from term I for $k_5 = k_5'$

$$\frac{k_5}{k_4} = \frac{2i(1 + \alpha) - (1 - \beta)}{1 - 2i}$$

where i is the intercept of the plots on the $1/\phi$ axis. The data of this Laboratory give $i = 0.14 \pm 0.1$.

The values assigned to α and β also determine in part the rate of increase of $1/\phi$ with $p_{\mathrm{O_2}}(p_{\mathrm{O_2}} + p_{\mathrm{O_3}})/p_{\mathrm{O_3}}$. Variations in the calculated value of $1/\phi$ for $\alpha = 0$ or 1 and $\beta = 1$ or 2, using corresponding values of k_5/k_4 determined from i, do not fall outside the limits of experimental error; hence, it is not possible to assign from the data unique values to α and β. The work of this Laboratory, however, gives $\phi > 4$ when $p_{\mathrm{O_2}}P/p_{\mathrm{O_3}}$ is less than 100. Therefore, β must be greater than zero; otherwise, if the postulated mechanism is correct, ϕ could not exceed 4 even though all the primary products of the photo dissociation subsequently decomposed ozone. A plausible assumption[9] is to set $\beta = 2$.

We may evaluate α in the following way. At λλ 208, 254, 280 and 313 mμ, the approximate equivalence of ϕ suggests that the primary act is essentially similar at these wave lengths, *i. e.*, α remains unchanged. The energy available at λ 313 mμ (91 kcal.) is sufficient to dissociate ozone into an oxygen atom and an oxygen molecule in its first electronically excited $^1\Sigma$ state (24 + 37 kcal.). It is not sufficient, however, to dissociate an ozone molecule into oxygen atoms (24 + 117 kcal.).[12] Also, the energy of the $^3\Sigma$ to $^1\Sigma$ transition, 37 kcal., corresponds almost exactly with the difference between the long wave length limits of the ultraviolet[6b] and visible[9] absorption spectra of ozone, λ 350 and λ 650 mμ, respectively, or 82–44 = 38 kcal. In addition the $^1\Sigma$ state of oxygen is metastable as evidenced by the very weak absorption of oxygen at λ 760 mμ corresponding to the transition $^3\Sigma$ to $^1\Sigma$. A plausible assumption, therefore, for absorption by ozone in the near ultraviolet is to set $\alpha = 1$. Thereupon, $k_5/k_4 = 2$ for $\alpha = 1$, $\beta = 2$ and $i = 0.14$.

The rate of arrival of the chain carriers at the

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(11) If the synthesis of ozone from oxygen atoms and ozone molecules were bimolecular, $[\mathrm{O_2}](k_3[\mathrm{O_2}] + k_3'[\mathrm{O_3}] + k_3S_3)$ in III would become $k_3''[\mathrm{O_2}]$. However, plots of $1/\phi$ with $p_{\mathrm{O_2}}/p_{\mathrm{O_3}}$ differ greatly at small mole fractions of ozone with changes in the initial pressure of pure ozone, thereby implying corresponding variations in the rate constants.

(12) Lewis and von Elbe, THIS JOURNAL, **57**, 612 (1935).

TABLE III

Serial number	λ in mμ	$\bar{P}$	$\bar{p}_{O_3}$	$\bar{p}_{O_2}$	$\bar{p}_{O_2}\bar{P}/\bar{p}_{O_3}$	$E_0 \times 10^{-16}$	Av. obsd. value of $1/\phi$	$\Delta(1/\phi)$	S_n	Term I	Term II	Calcd. value of $1/\phi$	$\Delta(1/\phi)$
3-7	254-2 Zn	525	222	303	716	*3.0*	*0.39*	*0.08*	12	0.28	0.11	*0.39*	*0.09*
3-6 3-8		524	224	300	700	*14.4*	*.47*		59	.28	.20	*.48*	
3-7 3-9		530	212	318	795	*3.3*	*.43*	*.10*	13	.29	.12	*.41*	*.11*
3-8		530	212	318	795	*16.8*	*.53*		64	.29	.23	*.52*	
$1/\phi$ calculated from Equation III; $\alpha = 1$; $\beta = 2$; $\frac{k_5}{k_4} = 2$; $\frac{2k_2}{k_3} = 7500$; $k^{7b} = 0.16$; $A = 6 \times 10^{-15}$													
3-3	208-4 Zn	493	286	207	357	*2.0*	*0.22*	*0.09*	9	0.22	0.05	*0.27*	*0.07*
3-2 3-4		491	290	201	340	*11.6*	*.31*		51	.23	.11	*.34*	
3-3 3-5		502	268	234	440	*2.1*	*.27*	*.14*	8	.24	.06	*.30*	*.09*
3-4		506	260	246	480	*12.0*	*.41*		47	.26	.13	*.39*	
$1/\phi$ calculated from Equation III; $\alpha = 1$; $\beta = 2$; $\frac{k_5}{k_4} = 2$; $\frac{2k_2}{k_3} = 7500$; $k^{7b} = 0.015$; $A = 5 \times 10^{-14}$													

wall determines S_n. It is, therefore, proportional to the concentration of oxygen atoms, [O], and excited oxygen molecules, [O_2'], and to their rate of diffusion to the surface, S. From equations I and II, [O] and [O_2'] are directly proportional to the concentration of absorbing ozone molecules, *i. e.*, to the incident light flux, E_0, multiplied by the fraction of light absorbed, or to[13]

$$E_0\left(1 - \frac{I}{I_0}\right) = E_0\,(1 - e^{-k'p_{O_3}d}) = E_0\left(k'p_{O_3}d - \frac{(k'p_{O_3}d)^2}{2!} + \frac{(k'p_{O_3}d)^3}{3!}\cdots\right) = E_0 f(k'p_{O_3}d)$$

where $k' = 2.3\ k$ = the absorption coefficient of ozone, and d is the depth of the absorbing layer.[14]

Their rate of diffusion according to the kinetic theory of gases, is inversely proportional to

$$1/D_{y-x} + 1/D_{y-z} + \ldots$$

where D_{y-x} is the diffusion coefficient of y in x. At constant temperature

$$D_{y-x}\ \alpha\ \frac{1}{\sigma^2_{y-x}\ p_x \left(\frac{1}{M_y} + \frac{1}{M_x}\right)^{-1}}$$

where σ^2_{y-x} is the sum of the radii of the respective molecules or atoms, M_y, M_x their respective masses and p_x is the partial pressure of x. Neglecting differences in σ and M, it follows that the rate of arrival of the chain carriers at the wall is

$$S_n = A_n E_0 f(k'p_{O_3}d)/P$$

The "constant" A_n depends among other things upon the temperature, the nature of the surface and the distribution of incident light flux over the surface. With our apparatus the latter varies widely with wave length. It is approximately constant, however, at a given wave length and temperature, for E_0 was diminished by stopping down the collimation lens; the slits and source were left unchanged.

As k_3S_3 and k_5S_5 enter equation III as additive terms to the total pressure, term I of III increases with E_0 and kp_{O_3}. Also, that part of term II of III containing k_3 in the numerator, briefly, $(k_3p_{O_2}P + k_2S_2)/(k_2p_{O_3} + k_2S_2)$ increases with k_2S_2 for all values of $k_3p_{O_2}P/k_2p_{O_3}$ less than 1. (When the latter exceeds 1, k_2S_2 is negligible for $S_n \longrightarrow 0$ as $P \longrightarrow \infty$; also $k_3/k_2 \ll 1$.) Equation III, with the above value for S_n is, therefore, in agreement with the observed secondary increase in $^1/\varphi$ or decrease in ϕ with increase in E_0 and extinction kp_{O_3} as it varies with wave length.

Table III gives the observed and calculated dependence of ϕ upon light intensity at λλ 254 and 208 mμ. Calculations are for $k_3 = k_3'$, $k_5 = k_5'$, $A_1 = A_2 = A_3$ and $f(k'p_{O_3}d) = k'p_{O_3}d$. With these approximations, calculated values of ϕ agree with those observed both with the change in ϕ with E_0 and in absolute magnitude. The calculations also show the inhibiting effect of the surface to be due mainly to reaction (k_2S_2). (The area of the beam incident on the reaction cell at λ 208 mμ, $A = 5 \times 10^{-14}$, was approximately ten times that at λ 254 mμ, $A = 6 \times 10^{-15}$.) The curves in Fig. 1 were similarly calculated

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[13] For all positive values of $k'p_{O_3}d$, $f(k'p_{O_3}d)$ is positive and increases with k'.

[14] When the surface effect becomes measurable, *i. e.*, when a measurable number of the chain carriers reaches the wall, d must be very small because the chains are short, $\phi_{max.} < 10$. Also, O and O_2' have lifetimes certainly less than the time to diffuse a millimeter at our pressures and temperatures. (There is no observable aftereffect.)

without change in k_3/k_2 or k_5/k_4. Between the earlier work,[1] Series 3, $A = 5 \times 10^{-14}$, and Series 5, $A = 1 \times 10^{-14}$, the double front window of the reaction cell was dismantled and the remaining inner window heated to softness.

The data of this Laboratory are, therefore, in complete accord with an energy chain mechanism for the photochemical decomposition of ozone in which (1) the surface acts as an inhibitor, (2) the chain carriers, oxygen atoms and excited oxygen molecules, have an average lifetime of the same order of magnitude as the time between collisions at our pressures and temperatures, and (3) the chain propagating reactions have a positive energy of activation (k_4/k_5 is less than unity).

The author is most grateful to Professor George Shannon Forbes for supplying the materials, apparatus and facilities of his laboratory for this research while the author was associated with him in the pursuit of other problems in photochemistry.

Summary

Initially pure dry ozone at 177 and 390 mm. was photolyzed at λλ 208, 254 and 313 mμ to complete decomposition.

Quantum yields, ϕ, referred to ozone molecules decomposed per quantum absorbed, were found approximately equivalent at 208 and 313 mμ.

The ten-degree temperature coefficient for the photolysis was found to be 1.15 ± 0.02 over the range 0 to 60° after ϕ was corrected for the dark reaction between pressure readings before and after photolysis. The coefficient is apparently independent of the mole fraction of ozone in oxygen and of the temperature interval, even when the dark rate was 20% of the total decomposition. In no case was there an observable after effect.

The ten-degree temperature coefficient for the dark rate over the range 20 to 60° was found to be 3 ± 0.1 for small mole fractions of ozone in oxygen.

Within the limits of experimental error, plots of $1/\phi$ against $p_{O_2}(p_{O_2} + p_{O_3})/p_{O_3}$ fall on smooth curves for which $1/\phi$ increases with this ratio. The decrease in ϕ with increase in light intensity and extinction kp_{O_3} as it varies with wave length at λλ 208, 254 and 280 mμ is secondary. At λ 313 mμ no such dependence of ϕ upon light intensity was observable.

Results, $\phi_{\text{max.}} > 4$ at all wave lengths, are quantitatively accounted for by the mechanism $O_3 + h\nu \longrightarrow O_2' + O$; $O + O_3 \longrightarrow 2O_2'$; $O + O_2 + M \longrightarrow O_3 + M$; $O + S \longrightarrow {}^1/_2\, O_2 + S$; $O_2' + O_3 \longrightarrow 2O_2 + O$; $O_2' + M \longrightarrow O_2 + M$, where M is any energy acceptor including the surface, S.

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The Rearrangement of Sugar Acetates by Aluminum Chloride. Further Studies on Neolactose and *d*-Altrose[1]

BY NELSON K. RICHTMYER AND C. S. HUDSON

In 1926, Kunz and Hudson,[2] by the action of aluminum chloride on a chloroform solution of lactose octaacetate, obtained the acetochloro derivative of a new disaccharide which they named neolactose. From acetochloroneolactose they prepared the neolactose α- and β-octaacetate; the free sugar was obtained in sirupy form by deacetylation of the α-octaacetate, and the equilibrium specific rotation[3] of neolactose in water was found to be approximately +35°. The structure of neolactose as *d*-galactosido-*d*-altrose was established by acid hydrolysis of the disaccharide and of its oxidation product, neolactobionic acid; the *d*-galactose was readily isolated in crystalline form, while the sirupy *d*-altrose portion was identified (1) through its phenylosazone, (2) through the brucine salt of *d*-altronic acid, and (3) by nitric acid oxidation to crystalline *d*-talomucic acid. It was found that the equimolecular mixture of *d*-galactose and *d*-altrose that results from the acid hydrolysis of neolactose rotates −8.95° in water, from which it follows, since *d*-galactose shows +80°, that the

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[1] Publication authorized by the Surgeon General, U. S. Public Health Service. Presented in part before the Division of Organic Chemistry at the New York Meeting of the American Chemical Society, April 22, 1935.

[2] Kunz and Hudson, THIS JOURNAL, **48**, 1978, 2435 (1926).

[3] Throughout the article the rotations are specific rotations at 20° for sodium light.