Important advantages pertain to the more dilute solution at the shorter wave lengths.

If uranyl oxalate is substituted for uranyl sulfate in both the above solutions the problem of purification is greatly simplified and ϕ remains unchanged. It also remains unchanged (except at λ208 mμ) in a solution containing 0.005 mole of uranyl oxalate and 0.0025 mole of oxalic acid per liter.

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The Photolysis of Dry Ozone at λ208, at λ254 and at λ280 mμ.   I.   Quantum Yields

By LAWRENCE J. HEIDT AND GEORGE S. FORBES

The purpose of this investigation was to study the photolysis of carefully purified dry ozone in monochromatic light over a wide range of temperature and of total and partial pressures of ozone and of oxygen. No foreign gases or vapors were added. As in our previous work[1] no stopcocks were used in the purification train, and mercury vapor was eliminated in the process. In all cases the resulting partial pressures of oxygen were caused by the decomposition of ozone.

Warburg[2] studied this photolysis over this wave length region but his observations were confined to ozonized oxygen at atmospheric pressure and room temperature, containing from 2 to 5% ozone. Further, the mechanism of photolysis which he proposed differs markedly from the energy chain mechanism of Kistiakowsky[3] and of Schumacher[4] based upon their observations of the photolysis in the visible[3,4a] and at λ313 mμ.[4b]

The apparatus, experimental procedure and precautions were essentially the same as those used by us in studying the influence of water vapor upon this photolysis.[1] Moisture was prevented from condensing on the window of the trapezoidal gas cell,[1] when the cell was cooled, by fusing on a second quartz window, 3 mm. from the front window and parallel to it. The space between the windows was evacuated to 10^{-5} mm. At λ208 mμ the air–quartz-air transmission of the outer window was 0.91 and the ratio of transmissions of the air–quartz–air interfaces of the *inner* window of the gas cell to the air–quartz–water interfaces of the actinometer cell was 0.93. A rectangular hole was cut in the side of a 400-cc. semi-transparent fused quartz beaker and the edges of this hole were fused to the edges of the inner front window of the cell. Thus the evacuated space and the front window were wholly outside the beaker. Temperature was controlled by means of water at 25°, or ice and water, or a mush of carbon dioxide snow and ethyl alcohol. With a small

electrical heater fitted between the exit slit of the monochromator and the gas cell and with proper thermal insulation, the front windows of the cell could be kept clear and the pressure in the cell at −80° held constant to 0.05 mm. of mercury for periods of over three hours. The temperature was recorded with a pentane thermometer graduated in millimeter intervals to 0.5°.

For purposes of actinometry a space of 5 mm. was provided between the exit slit and gas cell window for mounting the rectangular fused quartz actinometer cell (all seams fused) 30 × 70 × 5 mm. (inside measurements). A blast of air kept this cell at room temperature. This arrangement of course precluded the use of the thermopile–galvanometer system. Since the transmissions of the actinometer cell windows could not be determined separately without sawing the cell apart, the two windows were placed next the exit slit in alternate exposures. The average transmission air–quartz–water was then taken as the square root of the transmission of the entire cell filled with water at room temperature. During exposure a black paper was inserted between actinometer cell and gas cell. The actinometer solution used and the analytical procedure and precautions were the same as in the previous research.[1] Careful comparisons showed the quantum yield of this solution identical with that of the more concentrated solution standardized in this Laboratory. The "dark" reaction of ozone was followed before and after each photolysis, and found to be negligible over the time of any photolysis.

Four separate fillings of the gas cell were made, identified by the first serial numbers in the table. After each filling, the cell was cleaned with a hot sulfuric–nitric acid mixture, thoroughly washed, flamed and evacuated on the diffusion pump. Thereupon, ozone freshly purified by fractionation was introduced. The second serial number refers to a series of experiments under conditions approximately identical, and a small letter refers to an individual experiment. In the second column appears the average wave length with the number of spectral lines in the close group used for photolysis. All pressures were recalculated to 0°, in terms of mm. of mercury at 0°. P is the total pressure in the cell during a photolysis, ΔP the increase in P, and p_{o_3} and p_{o_2} partial pressures. An average is denoted by a bar over the symbol in question. All the quantum yields as given were multiplied by a constant factor 1.02 very nearly, to correct for the (estimated) dead space in the manometer and its capillary connections.

(1) Forbes and Heidt, THIS JOURNAL, 56, 1671 (1934).
(2) Warburg, Sitzb. preuss. Akad. Wiss., 644 (1913).
(3) Kistiakowsky, Z. physik. Chem., 117, 337 (1925).
(4)(a) Schumacher, ibid. 17B, 405 (1932). (b) Beretta and Schumacher, ibid., 17B, 417 (1932).

Results of the investigation are summarized in Table I. It is evident from the magnitude of ϕ that even in the absence of water vapor the reaction has chain characteristics, although it should be noted that ϕ is much smaller in the present case. Since ϕ frequently exceeds two, and in some cases four, any chemical chain mechanism such as that of Warburg now appears quite improbable. An energy chain mechanism such as

postulated by Kistiakowsky[3] and Schumacher[4] for the photolysis in the visible and near ultraviolet, now becomes plausible at these wave lengths also. Our values of ϕ, however, are much greater than any they observed. Likewise the tendency of ϕ to decrease with p_{O_2} when p_{O_2} is large is more nearly in accord with that observed by Warburg than that observed by Schumacher at 313 mμ.

TABLE I

Serial number	λ in mμ	$\bar{P}$	$\bar{p}_{O_3}$	$\bar{p}_{O_2}$	Cell temp., °C.	Quanta abs./min. $E \times 10^{-16}$	Time of photolysis, minutes	ΔP	ϕ
1-1	210-4	450	(428)	(22)	0.5	12.1	27	5.94	5.2
1-22		456	(416)	(40)	.5	12.4	26	4.53	4.1
2-1	210-4	349	(334)	(15)	.3	13.2	20	6.16	6.7
2-2		359	(314)	(45)	.3	12.2	21	4.56	5.1
2-3		364	(304)	(60)	.4	11.8	20	3.66	4.5
2-4a	210-4	369	(294)	(75)	21.0	11.0	20	2.68	3.6
b		373	(286)	(87)	24.1	13.0	18	3.49	4.2
c		378	(276)	(102)	25.2	11.0	21	5.03	6.3
2-5a	210-4	388	(256)	(132)	0.4	8.1	22	2.67	4.3
b		391	(250)	(141)	.5	8.1	22	2.62	4.3
c		393	(246)	(147)	2.4	7.7	20	2.12	4.0
3-1	210-4	445	382	63	.3	13.0	20	5.09	5.6
3-2a	210-4	475	322	153	27.7	10.5	20	2.91	4.0
b		479	314	165	27.7	11.5	20	2.75	3.6
c		487	298	189	26.1	12.0	21	2.99	3.4
3-3a	210-4	490	292	198	24.8	1.93	38	1.18	4.7
b		495	282	213	27.3	2.02	44	1.42	4.6
3-4a	210-4	505	262	243	23.7	12.7	21	2.09	2.3
b		507	258	249	23.1	11.4	18	1.76	2.5
3-5a	210-4	511	250	261	25.4	2.24	42	0.89	2.7
b		513	246	267	26.7	2.32	40.5	.93	2.8
3-6a	254-2	517	238	279	29.0	11.4	20	1.79	2.3
b		520	232	288	29.8	12.4	25	2.66	2.4
3-7a	254-2	524	224	300	24.5	3.04	41	1.13	2.6
b		526	220	306	24.6	3.04	49	1.33	2.6
3-8a	254-2	529	214	315	21.3	17.1	26	2.89	1.9
b		532	208	324	21.6	16.6	24	2.75	2.0
3-9a	254-2	534	204	330	22.1	3.58	46	1.32	2.3
b		536	200	336	21.6	3.50	46	1.04	1.9
3-10a	280-2	539	194	345	23.6	12.3	21	1.67	1.9
b		541	190	351	23.9	8.8	21	1.01	1.6
3-11a	280-2	542	188	354	22.6	1.71	42	0.28	(1.1)
b		543	186	357	22.8	1.74	43	.55	2.1
3-12a	280-2	544	184	360	21.4	8.9	26	1.44	1.8
b		546	180	366	21.7	9.05	21.5	1.25	1.8
3-13a	280-2	547	178	369	22.2	1.21	43	0.28	(1.5)
b		548	176	372	22.8	1.66	46.5	.10	(0.4)
3-14a	210-4	549	174	375	22.2	11.9	21	1.24	1.4
b		550	172	378	22.7	13.1	25	1.84	1.6
3-15a	210-4	552	168	384	23.1	1.08	40	0.40	2.7
b		553	166	387	22.5	0.54	47	.27	3.0
3-16a	210-4	554	164	390	23.4	12.1	23	1.28	2.1
b		556	160	396	23.4	9.0	20	1.19	1.9

TABLE I (Concluded)

Serial number	λ in mμ	$\bar{P}$	$\bar{p}_{O_2}$	$\bar{p}_{O_3}$	Cell temp., °C.	Quanta abs./min. $E \times 10^{-16}$	Time of photolysis, minutes	ΔP	φ
3-17a	210-4	562	148	414	26.2	7.7	20	1.02	1.4
b		563	146	417	25.9	11.7	22	1.50	1.7
3-18a	254-2	565	142	423	24.2	13.4	20	1.41	1.5
b		566	140	426	24.4	13.4	21.5	1.56	1.6
3-19a	280-2	569	134	435	23.9	7.6	21	1.04	1.9
b		570	132	438	24.5	6.9	22.5	0.80	1.5
3-20a	210-4	577	118	459	26.4	1.38	95	1.79	3.9
b		582	108	474	25.3	1.15	95	1.78	4.5
3-21a	210-4	580	112	468	25.4	12.0	20.5	1.28	1.5
b		581	110	471	25.4	11.5	24	1.28	1.3
3-22a	210-4	585	102	483	23.9	2.09	71	1.29	2.5
b		587	98	489	24.0	7.4	27.5	1.26	1.8
3-23a	280-2	588	96	492	24.3	5.12	25.5	0.91	2.0
b		586	100	486	24.5	7.16	26.5	1.02	1.6
3-24a	280-2	613	46	567	25.0	4.26	58.5	0.85	1.0
b		614	44	570	26.5	5.22	63.5	1.19	1.0
3-25a	210-4	615	42	573	25.1	6.83	61.0	2.00	1.4
b		617	38	579	25.8	8.40	40	1.54	1.3
3-26a	254-2	618	36	582	23.7	10.3	48.5	0.92	0.5
b		619	34	585	24.7	10.9	76	1.20	.4
4-1	210-4	227	178	49	27.0	8.25	25	3.43	4.9
4-2	210-4	244	144	100	24.4	7.81	38.5	2.52	2.4
4-3	210-4	245ᵃ	142	103	-80.0	6.00	99	0.86	0.4

ᵃ Calculated from P at 24°. $\gamma_{10^\circ} \phi = 1.18$. Partial pressures given in parentheses are estimated.

The dependence of φ upon light intensity is shown in Fig. 1 where $\log_{10} \phi$ at each of several wave lengths is plotted against $\log_{10} E$, where E is light flux in quanta per minute absorbed by ozone. It will be noticed that the lines are nearly parallel at a given wave length, but that as the wave lengths vary the slopes change, as do the extinction coefficients. A similar tendency was noted in the case of wet ozone.[1] In all such experiments p_{O_2} and p_{O_3} were large compared to Δp_{O_2} and Δp_{O_3} and the temperature was held fixed. The influences of p_{O_3} and p_{O_2} upon φ were eliminated in the plots by determining each slope with three series of observations: two series at one intensity (average denoted with closed circle) and in between these two series, a single series at another intensity, each observed value denoted by an open circle.

Since it is difficult to postulate a reaction mechanism in which φ is *directly* dependent upon light intensity, it is quite possible that the dependence of φ upon E is due to diffusion of the reactive products to the walls. In most of our experiments absorption was "complete" within a very small distance (1 mm.) from the front window, which should augment the relative importance of wall reactions.

Temperature Coefficient.—The average of experiments 2-4a, b, c at 23°, φ = 4.7, may be compared with 2-3 and 2-5, a, b, c, all at 0.4°, φ =

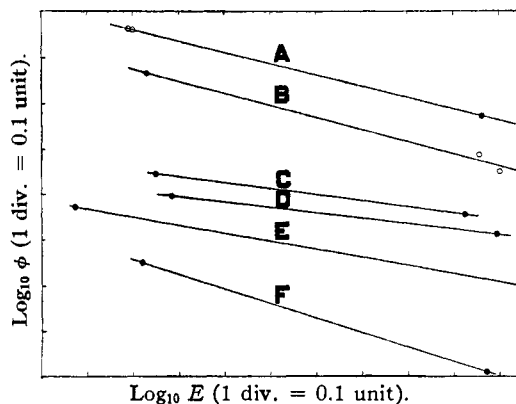Log₁₀ E (1 div. = 0.1 unit).
Fig. 1.

Curve	λ mμ	Experiments	Slope
A	210-4	3-2, 3-3, 3-4	-0.25
B	210-4	3-3, 3-4, 3-5	- .26
F	210-4	3-14, 3-15, 3-16	- .32
C	254-2	3-6, 3-7, 3-8	- .13
D	254-2	3-7, 3-8, 3-9	- .12
E	280-2	3-10, 3-11b, 3-12	- .18

4.3. It is regrettable that series 2-4 for reasons unknown is somewhat less reliable than the others. This comparison leads to a temperature coef-

ficient, $\delta_{10°}$ ϕ, only slightly exceeding unity. By analogy this tends to justify our interpretation of the quantum yields of moist ozone at 25 and 2°, respectively, that ϕ depends mainly upon the square root of the partial pressure of saturated water vapor, and that the effects, upon ϕ, of changing the temperature from 25 to 0° are otherwise negligible. On the other hand, one preliminary experiment (4–3) at −80° with temperature regulation as described above gives δ_{10} ϕ = 1.3 over the range 0 to −80°. Special experiments showed that the pressure in the cell was lowered less than 1% when a block of carbon dioxide snow placed against the front window was substituted for the heater. The quantum yields at −80° are therefore subject at least to a correction factor between 0.99 and 1.00. The value 1.3 may well be too low for the additional reason that the millimeter layer of gas next the inner front window, in which practically all the photolysis occurred, must have maintained a temperature higher than −80° owing to the proximity of the heater. A more detailed study of this apparently non-uniform temperature coefficient over the range 25 to −80° is desirable, as it might supply valuable clues regarding the kinetics of the reaction.

The dependence of ϕ upon total and partial pressures is strikingly similar to that observed in the case of wet ozone.[1] Again ϕ is found to increase with the partial pressure of ozone and to decrease with the partial pressure of oxygen. More evident, however, is the tendency of ϕ to decrease as the total pressure is increased suggesting that the chain-breaking three-body collisions involving regeneration of ozone from oxygen molecules and oxygen atoms and two-body deactivating collisions involving excited oxygen molecules are important.

For the present we would rather defer any detailed consideration of the mechanism of this photolysis.

Summary

The photolysis of carefully purified dry ozone has been studied at 208, 254 and 280 mμ. Molecules of ozone decomposed per quantum absorbed by ozone were as high as 6.7 = ϕ, indicating an energy chain mechanism.

Total pressures ranged from 230 to 620 mm. of mercury; partial pressures of ozone, p_{O_3}, and of oxygen, p_{O_2}, ranged from 35 to 430 mm. and from 15 to 585 mm., respectively.

A rough minimum value of the ten-degree temperature coefficient of ϕ, upon changing the temperature of the outside *bath* from 25 to −80° in a single experiment, was found to be 1.2.

The dependence of ϕ upon total and partial pressures, and upon light intensity was strikingly similar to that found in an earlier research in the presence of water vapor, but no direct dependence of ϕ upon wave length was noted.