[Contribution from the Frick Chemical Laboratory, Princeton University]

THE MECHANISM OF THE PHOTOCHEMICAL DECOMPOSITION OF OZONE

By Hans Joachim Schumacher[1]

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Introduction

Investigations concerning the photochemical decomposition of ozone have been presented by Regener,[2] E. v. Bahr,[3] Warburg,[4] Weigert,[5] Weigert and Böhm,[6] Griffith and Shutt,[7] Griffith and McWillie[8] and Kistiakowsky.[9] The results of their researches have been summarized by Kistiakowsky[9] and by Griffith and McKeown;[10] nevertheless, it is necessary to restate briefly the experimental facts before proceeding to a discussion of the mechanism.

Regener[2] has investigated the equilibrium of formation and decomposition of ozone in different regions of the ultraviolet light. The light source was an aluminum arc from which in one series of experiments all light of wave lengths $\lambda < 2100$ Å. was filtered out by a plate of calcite. As he was not particularly interested in the kinetics of the reaction, his velocity measurements are incomplete and only roughly quantitative. Nevertheless, it can be estimated that for constant light absorption the velocity of decomposition is nearly proportional to the ozone concentration. It is important to note that a positive temperature coefficient for the decomposition of ozone was obtained at total pressures of 1 atm., of which about 1–5% was ozone and the rest oxygen.

E. v. Bahr[3] has worked with highly dilute mixtures of ozone, the pressure of which was usually of the order of 1 mm. of mercury or less. The total radiation of a mercury lamp was used and the ozone concentration determined by optical measurements. Her data can be used only qualitatively because experiments of the same kind deviate from each other by about 100% due to neglect of a dark reaction, and the inaccurate method of analysis. Nevertheless, her results are important. E. v. Bahr finds that the quantum yield increases very markedly with decreasing pressure. (She measured only the velocity of the reaction, but the quantum yield and velocity

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[1] International Research Fellow.

[2] Regener, *Ann. Physik*, **20**, 1033 (1906).

[3] E. v. Bahr, *ibid.*, **33**, 589 (1910).

[4] Warburg, *Sitzb. preuss. Akad. Wiss.*, 644 (1913).

[5] Weigert, *Z. physik. Chem.*, **80**, 87 (1912).

[6] Weigert and Böhm, *ibid.*, **90**, 233 (1915).

[7] Griffith and Shutt, *J. Chem. Soc.*, **123**, 2752 (1923).

[8] Griffith and McWillie, *ibid.*, **123**, 2762 (1923).

[9] G. B. Kistiakowsky, *Z. physik. Chem.*, **117**, 337 (1925).

[10] Griffith and McKeown, "Photoprocesses in Gaseous and Liquid Systems," Longmans, Greene and Co., London, **1929**.

under the same conditions are, of course, proportional to each other.) At a total pressure of 20 mm. of mercury the reaction is ten to twenty times more rapid than at one atmosphere.

Weigert[5] has also investigated the decomposition of ozone in the ultraviolet, his light source being a mercury arc. The total pressure was always one atmosphere and the concentration of ozone varied from 0.9–6%. He found that when all light was absorbed, the order of the reaction was about one, whereas when the concentration of ozone was small, so that the light was not completely absorbed, the order of the reaction increased.

Weigert and Böhm[6] also studied the influence of hydrogen on the reaction and observed that the velocity of the decomposition of ozone was greatly increased. In the presence of a large excess of hydrogen the reaction rate was changed five- to ten-fold and water was formed.

Griffith[7] and co-workers have studied the decomposition of ozone in the visible range in the presence of oxygen and foreign gases at total pressures of 1 atm. When the oxygen was replaced by helium, nitrogen or carbon dioxide the velocity increased in the order $O_2 \longrightarrow N_2 \longrightarrow CO_2 \longrightarrow He$. Kistiakowsky[9] has shown that all gases inhibit the reaction, the inhibiting influence decreasing in the order given.

Hydrogen, according to Griffith, shows qualitatively the same influence on the reaction in the visible that Griffith and Böhm found in ultraviolet light, *i. e.*, the rate of decomposition of ozone increases and water is formed.

Heretofore these results were not of much use in the development of theories to explain the reaction because monochromatic light was not used, quantum efficiencies were not determined and the other experimental conditions were not varied sufficiently. Kistiakowsky[9] has given an empirical equation for the representation of some of these results.

Quantum yields for the decomposition of ozone in monochromatic light have been determined by Warburg[4] in the ultraviolet and by Kistiakowsky[9] in the red region. The important result of Warburg's work is that at a total pressure of 1 atm. and a partial pressure of a few mm. of ozone, the quantum efficiency is, with oxygen as added gas, about 0.30 mol. $O_3/h\nu$, with nitrogen 1.09 and with helium 1.70.

Most of the experimental facts upon which the following theoretical considerations are based are found in the work of Kistiakowsky,[9] for he varied the total pressure as well as the concentrations of the gases over a wide range and, which is more important, in his experiments the thermal decomposition of ozone was eliminated or could be estimated approximately. The velocity obtained by Warburg[4] in ultraviolet light always included a dark reaction whose rate was not determined and, as will be shown later, this is of particular importance in explaining some of his results.

The Decomposition of Ozone in Red Light.—To express the experimental data obtained in red light, Kistiakowsky has given the empirical equation

$$-\frac{d[O_3]}{dt} = \frac{k\,I_{abs.}\,[O_3]^{1/2}}{m[X] + [O_2]}$$

in which X denotes the concentration of the added gas and m a factor less than one. The equation is valid over only a limited range of pressure and concentration; at low total pressures, for example, the velocity is nearly proportional to $I_{abs.}$. Later unpublished experiments of Kistiakowsky,[11] which represent the course of the reaction in a more satisfactory manner because of better energy measurements and the more accurate determination of the final ozone concentration, show still more pronouncedly that the given equation can be used over only a limited range. On the other hand, since it is impossible to represent the reaction by a simple equation, it must be assumed that this can be done only by an equation of several terms.

It is characteristic of the decomposition in red light that the quantum yield, even at high ozone concentration, is relatively small. The greatest values of the quantum yield are between 2 and 3 moles $O_3/h\nu$ and are obtained at relatively low total pressures and high ozone concentration.[12] At high total pressures the quantum yield decreases and at 1 atm. pressure with 50% ozone it is less than unity (Experiment 3).[12]

At total pressures below 10 mm. the quantum yield is nearly 2. In the presence of 1–2 mm. of oxygen and 8–9 mm. of ozone it is about 2.5 and in the presence of 8–9 mm. of oxygen and 1–2 mm. of ozone it is about 1.5 (unpublished experiments of Kistiakowsky). It must be emphasized that greater velocities can also be obtained at higher total pressures if oxygen is replaced by foreign gases. According to Kistiakowsky, on the basis of oxygen equal to 1, the inhibiting action of helium is represented by 0.13, nitrogen 0.3 and carbon dioxide 0.8. The essential facts already given should readily follow from the mechanism of the reaction.[13]

It is of considerable importance to know whether to assume for the primary reaction the formation of an excited molecule of ozone or an atom of oxygen. Before treating the energy relations and the ozone spectrum we shall see which of the two possibilities should be selected from the ki-

[11] These experiments were carried out in 1925 by Dr. Kistiakowsky in the Kaiser Wilhelm Institut für Physikalische Chemie in Berlin, but could not be interpreted at that time and therefore were not published.

[12] Kistiakowsky, *Z. physik. Chem.*, **117**, 348 (1925).

[13] In this treatment a chain will be regarded as formed when more than 2 molecules of ozone react per quantum absorbed. We shall find that the measured quantum yield is not necessarily identical with the number of ozone molecules which react per quantum absorbed because ozone may also be regenerated. In spite of this difference the experimentally determined quantum yield, whose usual value is considerably less than 2, shows that there are often no chains or only a few short ones. Consequently, we can neglect chain formation without seriously limiting the validity of the theoretical treatment.

netics of the reaction. If we assume for the primary reaction the formation of an excited ozone molecule

$$O_3 + h\nu \longrightarrow O_3' \qquad (1)$$

we have only a limited number of possible reactions that may follow, namely

$$O_3' + O_3 \longrightarrow 3O_2^* \qquad (2)$$
$$O_3' + O_3 \longrightarrow 2O_3 \qquad (3)$$
$$O_3' + O_2 \longrightarrow O_3 + O_2 \qquad (4)$$

Reaction 2 may start a chain if we assume that the energy-rich oxygen molecule (O_2^*) can excite an ozone molecule. For reasons previously given we shall, however, neglect the formation of chains. Reactions 3 and 4 indicate the deactivating influence of the two gases. From this mechanism the following equation is derived

$$-\frac{d[O_3]}{dt} = \frac{I_{\text{abs.}}\,[O_3]}{(k_2 + k_3)[O_3] + k_4[O_2]}$$

If a foreign gas X is present, another term $k_5[X]$ is added to the denominator. From this equation it is evident that the total pressure should have no influence. If the oxygen–ozone ratio is constant, the quantum yield should be independent of the pressure. This is contrary to the experimental facts and, since on the assumption of excited molecules there are no other possible reactions than those already given, the formation of excited ozone molecules in the investigations previously discussed must be rejected. Thus we see that kinetic considerations lead us to assume the formation of oxygen atoms in the primary reaction.

We shall now consider the energy relations involved. The work of G. Herzberg[14] and R. Mecke[15] shows that the heat of dissociation of oxygen is below 6 volts; the value given by Mecke is 128,000 cal. per mole. The heat of decomposition of ozone is 32,000 cal. per mole. The minimum energy required by the reaction

$$O_3 \longrightarrow O_2 + O$$

is, therefore, only $(128{,}000/2) - 32{,}000 = 32{,}000$ cal., while the energy of the red light is more than 40,000 cal. (In the experiments of Kistiakowsky the mean absorption was at 6200 Å.) Of course, absorption of light of greater energy than the heat of dissociation does not necessarily require the dissociation of the molecule. This depends on the nature of the spectrum, as was first shown by Franck and his co-workers.

The ozone spectrum[16] consists of very diffuse bands in the red so that we may assume that predissociation[17,18] occurs even at these wave lengths.

[14] G. Herzberg, *Z. physik. Chem.*, **4B**, 223 (1929).

[15] R. Mecke, *Naturwissenschaften*, **51**, 596 (1929).

[16] Private communication from Dr. O. R. Wulf, who is now investigating the ozone spectrum.

[17] V. Henri, *Nature*, December 20, 1924; *Trans. Faraday Soc.*, **25**, 765 (1929).

[18] Bonhoeffer and Farkas, *Z. physik. Chem.*, **132**, 235 (1928).

These considerations show that the reaction

$$O_3 + h\nu \longrightarrow O_2 + O$$

is quite probable. Neglecting the formation of chains, only the following reactions are possible

$$O_3 + h\nu \longrightarrow O_2 + O \qquad (1)$$

$$O + O_3 \longrightarrow 2O_2^* \qquad (2)$$

$$O + O_2 + M \longrightarrow O_3 + M \qquad (3)$$

Reaction 2 can lead to chain formation. Equation 3 is a three-body reaction where M designates the third body. In the presence of little ozone and much oxygen, the oxygen pressure may be regarded as equivalent to M. If oxygen is replaced by helium, nitrogen or any other gas, M is represented by the pressure of this gas. In polyatomic gases a first approximation for M is given by the total pressure of the mixture, since ozone has influence also. The effect of various gases is specific, due to their difference in structure and specific ability to take up internal energy by collision; but polyatomic molecules are nearly the same in this respect and differ from each other generally by a factor less than 3.

From the preceding mechanism the following equation is derived

$$-\frac{d[O_3]}{dt} = I_{abs.} + k_2[O][O_3] - k_3[O][O_2][M]$$

$$[O] = \frac{I_{abs.}}{k_2[O_3] + k_3[O_2][M]}$$

$$-\frac{d[O_3]}{dt} = I_{abs.}\left[1 + \frac{k_2[O_3]}{k_2[O_3] + k_3[O_2][M]} - \frac{k_3[O_2][M]}{k_2[O_3] + k_3[O_2][M]}\right] \qquad (I)$$

Equation I should represent the experimental facts previously mentioned. It can be regarded as a first approximation since chain formation has been neglected.

Of course, Equation I can be written

$$-\frac{d[O_3]}{dt} = I_{abs.}\left(\frac{2k_2[O_3]}{k_2[O_3] + k_3[O_2][M]}\right) \qquad (II)$$

Since Equation I illustrates the mechanism better, it will be used in the following discussion.

When the ozone concentration is small and is held constant, *e. g.* $[O_3] <$ 10 mm. of mercury, and the total pressure is decreased (which means also decreasing the oxygen pressure), the third term of the equation becomes smaller and smaller and the second term approaches unity. For the limit we have

$$-\frac{d[O_3]}{dt} = I_{abs.}\ [1 + 1] \quad \text{or}$$

$$\frac{-\frac{d[O_3]}{dt}}{I_{abs.}} = 2 \text{ (Quantum Yield)} \qquad (III)$$

This case corresponds to Expts. 11 and 12 in the paper of Kistiakowsky (p. 149). The equation (I) shows that in this region the quantum yield is strongly influenced by pressure. With a small increase of $[O_2]$ and $[M]$ the negative term can no longer be neglected. Experiments 10 and 12 of Kistiakowsky illustrate this point; some of his unpublished experiments bring it out still more clearly. Furthermore, the experiments show that at low total pressures and very small concentrations of oxygen the quantum yield is greater than 2. This is to be expected from the proposed mechanism for under these conditions chain formation according to Reaction 2 is strongly favored. In the presence of more oxygen the activated molecules may be deactivated, so the probability of forming a chain is decreased.

Let us now consider a high total pressure and a small concentration of ozone. In this case we have

$$k_2[O_3] < k_3[O_2][M]$$

Then the equation becomes

$$-\frac{d[O_3]}{dt} = \frac{2\,I_{abs.}\,k_2[O_3]}{k_3[O_2][M]} \qquad (IV)$$

In consequence of the small $[O_3]$, the total pressure and the oxygen concentration can change only to a slight extent during the reaction, which means that the denominator of Equation IV becomes constant and the rate of ozone decomposition can be given by the simple equation

$$-\frac{d[O_3]}{dt} = k\,I_{abs.}\,[O_3]$$

This case was realized in the work of Griffith and Shutt, who found that at total pressures of one atmosphere and small ozone pressures the reaction follows the equation

$$-\frac{d[O_3]}{dt} = k[O_3]^2$$

In their experiments the light absorption was proportional to the ozone concentration; hence these two equations become identical. Griffith and Shutt found at higher ozone concentration (above 5%) a decrease in the order of the reaction, which is a necessary consequence of Equations I and II. The two other limiting cases are those in which the total pressure and ozone concentration are both large or both small. In the former case with ozone concentration above 90%, a quantum yield greater than 2 should be found. At high pressure the greatest ozone concentration used was about 60% and here, as can be predicted, the quantum yield was considerably less than 2.[19] In the experiments with total pressures below 10 mm. of mercury, the quantum yield becomes much less than 2 if the ratio of oxygen to ozone is greater than five.[20]

If middle values for the oxygen and ozone pressures are employed instead of the extreme concentrations in the cases discussed above, then for con-

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[19] Kistiakowsky, Ref. 9, p. 345, Expts. 2, 3 and 5.

[20] Kistiakowsky, Ref. 9, p. 349, Expts. 10, 11, 12. The unpublished data show that the quantum yield is about 20% too low.

stant light absorption it is to be expected from Formula I or II that the dependence of the velocity on the ozone concentration will vary as $[O_3]^0$ to $[O_3]^1$. As can be readily seen from Equation II, inhibition by oxygen is nearly proportional to its concentration, for the total pressure [M] is $[O_3 + O_2]$ and so, as a first approximation, the whole denominator is proportional to $[O_2]^1$. Therefore we get

$$-\frac{d[O_3]}{dt} = k\frac{I_{\text{abs.}}\ [O_3]^{1/2}}{[O_2]}$$

which is identical with the empirical equation of Kistiakowsky.

As is shown by his unpublished work, the limits within which the equation holds are smaller than originally stated by Kistiakowsky. This is in agreement with our deduction of the above equation as a zero approximation.

There are difficulties involved in obtaining the exact mathematical representation of the velocity of decomposition of ozone over the whole range of pressures, for we know only little about the formation of the chains and the deactivation of the energy-rich oxygen molecules by ozone and oxygen. Furthermore, the value of the constant k_3 changes with the composition of the mixture. However, the course of the reaction is essentially represented by Equations I or II and the ratio of the velocity constants of Reactions 2, $O + O_3 \longrightarrow 2O_2$, and 3, $O + O_2 + M \longrightarrow O_3 + M$, can be calculated. The reaction $O + O_2 \longrightarrow O_3$, which requires a three-body collision, occurs at every 10^3 to 10^4 collision at atmospheric pressure, if we assume that no heat of activation is necessary and the third body is well adapted for taking up the excess energy. Then we have[20a]

$$k_3 = \frac{1}{10^3 \times 760}$$

if the total pressure is given in mm. of mercury (in place of 10^3, 10^4 may be used). If ozone and oxygen are well adapted for taking up the excess energy, the above value of k_3 may be used in our general equation. That oxygen is capable of so doing is shown by experiments on the quenching of fluorescence,[21,22] for which oxygen is especially efficient. Likewise, from observations on the prevention of explosions in mixtures of bromine and ozone[23] by oxygen we must conclude that the oxygen molecule is extraordinarily able to take up and dissipate the heat of reaction.

From Equation II we get for k_2

$$k_2 = \frac{[O_2][M]\,E}{760 \times 10^3 \times (2 - E)[O_3]}$$

[20a] In the following discussion k_2 and k_3 are the ratio of the velocity constants to the number of two-body collisions, that is, k_2 and k_3 give the probability that reaction occurs on collision.

[21] Wood, "Physical Optics," The Macmillan Company, **1923**, p. 581.

[22] Norrish, *J. Chem. Soc.*, 1604, 1611 (1929).

[23] Lewis and Schumacher, *Z. Elektrochem.*, **35**, 348 (1929); *Z. physik. Chem.*, **6B**, 423 (1930).

where $E = (-d[O_3]/dt)/I_{abs.}$, which is the experimentally determined quantum yield. The values for k_2 in the following experiments have been calculated by means of the above equation.

TABLE I

EXPERIMENTS OF KISTIAKOWSKY[a]

E = Quantum yield. The pressures of O_3 and O_2 are given in mm. of mercury

Expt. 2

O_3	O_2	P_{total}	E	$k_2 \times 10^3$	
271	215	486	1.06	0.58	
257	236	493	0.89	.50	
209	308	517	.73	.64	
167	371	538	.47	.48	k mean = 5.4×10^{-4}
153	392	545	.44	.51	
132	423	555	.36	.51	
51	544	595	.17	.70	

Expt. 4

O_3	O_2	P_{total}	E	$k_2 \times 10^3$	
167	90	257	1.5	0.55	
144	125	269	1.3	.58	
131	144	275	1.2	.59	
98	193	291	0.81	.60	
60	250	310	.51	.58	k mean = 5.8×10^{-4}
57	255	312	.44	.52	
27	300	327	.30	.49	
23	306	329	.23	.68	
20	311	331	.19	.67	

Expt. 5

O_3	O_2	P_{total}	E	$k_2 \times 10^3$	
139	95	234			
133	104	237	1.4	0.53	
126	114	240	1.2	.43	
112.5	135	247.5	1.05	.43	
78	185	263	0.71	.45	k mean = 4.6×10^{-4}
55	221	276	.45	.47	

UNPUBLISHED EXPERIMENTS OF KISTIAKOWSKY

Expt. 1

O_3	O_2	P_{total}	E	$k_2 \times 10^3$
326	144	470		
317	158	475	1.4	[0.68]
295	191	486	1.2	.54
288	202	490	1.1	.53
281	213	494	1.0	.47
273	225	498	0.9	.43
256	249	505	.8	.40
247	262	509	.7	.37
220	303	523	.6	.35
180	363	543	.43	.36
160	393	553	.40	.40
145	415	560	.33	.41
133	432	565	.30	.40

TABLE I (*Continued*)

O_3	O_2	P_{total}	E	$k_2 \times 10^3$	
113	462	575	0.29	0.48	
101	480	581	.25	.47	
89	498	587	.22	.49	
80	512	592	.21	.54	
55	550	605	.14	.46	k mean = 4.5×10^{-4}
		Expt. 2			
212	102	314	...	...	
204	114	318	1.4	0.50	
199	122	321	1.3	.46	
189	137	326	1.22	.45	
186	141	327	1.10	.39	
175	158	333	1.00	.36	
166	171	337	0.95	.38	
155	188	343	.85	.37	
151	194	345	.75	.34	
142	207	349	.70	.34	
133	220	353	.65	.35	
124	234	358	.60	.36	
92	282	374	.45	.33	
80	300	380	.35	.36	
61	328	387	.29	.38	
51	343	394	.26	.46	
50	345	395	.25	.50	k mean = 4.0×10^{-4}
		Expt. 4			
141	92	233	...	...	
138	96	234	1.40	0.48	
127	112	239	1.30	.45	
122	119	241	1.20	.44	
118	125	243	1.10	.43	
110	137	247	1.00	.37	
106	143	249	0.88	.35	
102	149	251	.82	.32	
97	157	254	.77	.32	
91	166	257	.73	.33	
86	174	260	.67	.33	
81	181	262	.67	.37	
77	187	264	.57	.32	
74	191	265	.51	.30	
67	202	269	.49	.31	
64	206	270	.47	.36	
61	211	272	.44	.33	
59	214	273	.42	.34	
57	217	274	.41	.34	
44	236	280	.33	.36	
37.5	247	284.5	.31	.40	
36	249	285	.29	.43	
27	265	292	.22	.36	
25	268	293	.22	.46	k mean = 3.7×10^{-4}

TABLE I (*Concluded*)

O_3	O_2	P_{total}	E	$k_2 \times 10^3$	
Expt. 6					
329	207	536			
315	228	543	1.1	0.58	
307	240	547	1.0	.54	
295	258	553	0.9	.49	
282	278	560	.8	.45	
259	309	567	.7	.43	
240	337	577	.6	.42	
229	354	583	.57	.45	
210	380	590	.50	.43	
195	402	597	.50	.50	
181	423	604	.43	.45	
174	434	608	.40	.48	
141	486	627	.25	.50	
128	506	634	.30	.54	
123	513	636	.27	.53	
97	552	649	.20	.44	
93	558	651	.21	.58	
90	562	652	.17	.48	
79	579	658	.16	.51	k mean $= 5.0 \times 10^{-4}$
Expt. 7					
90	70	160			
88	73	161	1.4	0.40	
84	79	163	1.3	.35	
78	88	166	1.2	.34	
70	100	170	1.0	.28	
67	104	171	0.95	.31	
61	113	174	.90	.32	
59	116	175	.86	.32	
54	124	178	.76	.30	
51	128	179	.73	.32	
49	131	180	.69	.32	
47	134	187	.70	.35	
45	137	182	.66	.35	
44	139	183	.65	.36	
32.5	156	183.5	.55	.36	
31	159	190	.55	.47	
29.5	161	191.5	.49	.43	k mean $= 3.5 \times 10^{-4}$

[a] *Z. physik. Chem.*, **117**, 345 (1925).

It is to be seen that the values of k_2 are fairly constant when $E < 1.5$. Higher values of E indicate the formation of chains and in this region our equation is no longer correct. Furthermore, k_2 gradually increases toward the end of the experiment, which is to be accounted for by the fact that k_3 is assumed to be constant, whereas it really changes with the composition of the mixture. When it is considered that for the calculation of k_2 the quantum efficiency E has been used, and that the error in E is about 10 to

20%, it is realized that the constancy of k_2 is very good. For high values of E (E near 2), large deviations in k_2 are to be expected, because in the equation we have as a factor the difference ($2-E$). The mean value for k_2 in Expts. 2, 4 and 5 is $[(5.7 + 5.8 + 4.6)/3]\ 10^{-4} = 5.4 \times 10^{-4}$; in Expts. 1, 3, 4, 6 and 7, $(4.5 + 4.0 + 3.7 + 5.0 + 3.5)/5 = 4.2 \times 10^{-4}$. In the two cases different light sources were used, which may easily account for the difference in the mean values of k_2. The intensity measurements were more accurate in the unpublished experiments. We have, therefore, to assume for k_2 about 5×10^{-4}, which means that the reaction $O + O_3 \longrightarrow 2O_2$, in which O is a normal atom, occurs only on every 2000th collision. We have the important result that a highly exothermic "Elementarreaktion" does not take place on every collision.[24] Recently two other similar cases have been pointed out by Kistiakowsky.[25] The probability of the occurrence of the reactions $Cl + H_2 \longrightarrow HCl + H$ and $O + H_2 \longrightarrow OH + H$ is also less than 10^{-3}.

The Influence of Foreign Gases.—When oxygen is replaced by foreign gases which do not react with ozone, the quantum efficiency is always greater than that obtained with oxygen. The influence of helium is extraordinarily remarkable, for its inhibiting effect is only $^1/_8$ that of oxygen. From the experiments of Jost[26] it is found that the recombination of bromine atoms is only slightly favored by helium. Hence, it may be readily assumed that also in the case of ozone the effect of helium is given by its influence on the efficiency of the three-body reaction $O + O_2 \longrightarrow O_3$. If helium is the third body the efficiency of the reaction may be one order of magnitude less than with oxygen. The effect of the other foreign gases may depend upon the same phenomenon. Recently it has been shown that the recombination of chlorine atoms[27] is less favored by nitrogen than by oxygen, and similarly in the case of ozone the effect of nitrogen is noticeably less than that of oxygen.

Another argument for the correctness of the idea developed is found in a comparison of the light reaction with the thermal[28] reaction. For the dark reaction the primary process is

$$O_3' + O_3 \longrightarrow 3O_2$$

where O_3' represents a thermally excited ozone molecule. The heat of activation of the thermal reaction is about 28,000 cal. If we assume that there are also excited ozone molecules in the photochemical reaction, then we should expect that foreign gases in both cases would have the same

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[24] H. Beutler and M. Polanyi, *Z. physik. Chem.*, **1B**, 1 (1928).

[25] G. B. Kistiakowsky, This Journal, **52**, 1868 (1930). See also H. J. Schumacher, forthcoming article in *Z. physik. Chem.*, Abt. B.

[26] Jost, *ibid.*, **3B**, 95 (1929).

[27] M. Bodenstein, H. J. Schumacher and G. Stieger, *ibid.*, **6B**, in press.

[28] H. J. Schumacher and G. Sprenger, *ibid.*, **6B**, 447 (1930).

effect. However, just the contrary is found. In the thermal reaction all foreign gases accelerate the decomposition, the velocity increasing with increased pressure of the added gas. The acceleration is the smallest for helium. In the light reaction, as previously indicated, it is quite different. All foreign gases inhibit the reaction, the velocity of which decreases in proportion to the amount of the added gas. The inhibiting effect of helium is the smallest. Compared with the oxygen experiments the velocity increases because the inhibiting influence of oxygen is extraordinarily large. By the assumption that in the photochemical reaction oxygen atoms are formed whereas the thermal reaction involves excited molecules, the different behavior in the two cases can be satisfactorily explained.[28]

The Reaction with Hydrogen.—The thermal reaction is only slightly influenced by hydrogen, while in the photochemical reaction, in the red as well as in the ultraviolet, the rate is greatly increased and water is formed.[29] The difference in behavior with respect to hydrogen in the thermal and photochemical reactions may be explained by assuming that excited ozone molecules do not react with hydrogen whereas oxygen atoms react.[30] Yet the reaction $O + H_2 \longrightarrow OH + H$, where O is a normal oxygen atom, occurs only very seldom as was shown by the experiments of Kistiakowsky and my own observations.[31] However, it may be assumed that water is formed according to the reaction $O + O_2 + H_2 \longrightarrow H_2O + O_2$, which is in agreement with the experiments of Weigert, and Griffith and Shutt. They found that in the presence of much hydrogen the rate of water formation becomes constant and practically all of the oxygen formed by the decomposition of ozone is transformed into water. We may have, therefore, for the predominant reactions

$$O_3 + h\nu \longrightarrow O_2 + O \qquad (1)$$

$$O + O_2 + H_2 \longrightarrow H_2O + O_2 \qquad (2)$$

The decomposition of ozone is strongly decreased by Reaction 2, since the reaction $O + O_2 + M \longrightarrow O_3 + M$, which regenerates ozone, is suppressed. The quantum efficiency in the investigated region in the absence of hydrogen is very small, hence a ten-fold increase in the velocity by hydrogen is not surprising. In the ultraviolet, where excited oxygen atoms are formed, the reaction $O + H_2 \longrightarrow OH + H$ may also occur.[9] Our present knowledge of the reactions $O + H_2$ and $O_2 + H_2$, however, is not sufficient to give with certainty the real mechanism of water formation.

The Effect of Temperature.—According to the proposed mechanism there should be no or only a very small temperature coefficient at low pressures where three-body collisions (Reaction 3) would seldom occur and

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[29] Griffith and Shutt, *J. Chem. Soc.*, **123**, 2572 (1923); Weigert, *Z. physik. Chem.*, **90**, 223 (1915).

[30] Farkas, Goldfinger and Haber, *Naturwissenschaften*, **17**, 674 (1929).

[31] H. J. Schumacher, forthcoming article in *Z. physik. Chem.*, (1930).

where the oxygen atoms, therefore, would always have an opportunity for reacting with ozone molecules. At higher pressures, however, a small but larger temperature coefficient should be found, because the reaction $O + O_2 + M \longrightarrow O_3 + M$ is practically independent of temperature, while the reaction $O + O_3 \longrightarrow 2O_2$ must be influenced by temperature. The unpublished experiments of Kistiakowsky show an increase of the temperature coefficient in the expected direction. (As was pointed out in the introduction, a small positive temperature coefficient at high pressures was also found by Regener.)

In conclusion, it may be said that the decomposition of ozone in red light is satisfactorily represented by the mechanism given.

The Decomposition of Ozone in Ultraviolet.—An exact interpretation of the decomposition of ozone in ultraviolet light is rather difficult because of the scarcity of quantitative data. Kistiakowsky has already pointed out the analogy between the reactions in red and ultraviolet light. There are only two important differences: (1) the higher quantum efficiency in the ultraviolet—the only available experiments are with small concentrations of ozone at atmospheric pressure and here the quantum yield is ten times that obtained in red light under the same conditions; (2) the influence of water vapor. According to Warburg[4] the decomposition of ozone is more rapid in the presence of moisture, whereas Kistiakowsky, in the red, observed no difference in behavior of dry or wet gases. By analogy with the reaction in the red and because of the fact that the absorption spectrum contains very diffuse bands, we may assume that the primary process in the ultraviolet is also $O_3 + h\nu \longrightarrow O_2 + O$. The acceleration of the reaction rate by a decrease in pressure, observed by E. v. Bahr,[3] may then be readily explained. At low pressures the reaction $O_2 + O + M \longrightarrow O_3 + M$, which removes oxygen atoms and regenerates ozone, occurs less often since it requires a three-body collision. This is, of course, equivalent to an increase in the velocity of decomposition. The influence of nitrogen and helium, both of which increase the quantum yield compared with oxygen, is to be explained in the same manner as for the reaction in red light, *i. e.*, nitrogen and especially helium are less adapted than oxygen in taking up the energy in a three-body collision.

The higher quantum efficiency in the ultraviolet may be explained in the following way. In the red we must expect that by the reaction $O_3 + h\nu \longrightarrow O_2 + O$ only a normal oxygen atom is formed, whereas in the ultraviolet the oxygen atom can contain much more energy, for the difference in energy between red ($\lambda \sim 620$ Å.) and ultraviolet ($\lambda \sim 2537$ Å.) is about 70 cal. Consequently, the reaction $O_3 + O \longrightarrow 2O_2$ which, as has been previously pointed out, occurs at every 2×10^3 collision, can now take place more frequently. From Warburg's experiments it can be calculated that the probability of the occurrence of this reaction is about 5×10^{-2}, assuming that the reaction $O + O_2 + O_2 \longrightarrow O_3 + O_2$ at a pressure of 1 atm. occurs at every 10^3 collision.

The reaction $O + O_3 \longrightarrow 2O_2^*$ is the only one that can initiate chains; therefore, the probability of chain formation is greater in the ultraviolet, where this reaction takes place more frequently than in the red. Another reason for the high velocity in the ultraviolet is to be found in the fact that the reaction of ozone with an excited oxygen atom can form oxygen molecules with 80 cal. excess energy, while in the reaction with a normal atom the excited oxygen molecule may have at the maximum 50 cal., since it is quite plausible to assume that the probability that ozone is excited by an oxygen molecule for reaction or decomposition is increased with increase in energy content of the latter. From the above considerations the higher quantum efficiency in the ultraviolet light is readily understandable. Warburg found at a total pressure of 1 atm., 90% O_2 and 10% O_3, the quantum yield 3.5.

It is impossible to discuss the chains in detail since the behavior of concentrated ozone mixtures needs to be known and no experiments in this region are available.

The author has set up equations for $d[O_3]/dt$ for every possible reaction scheme considering the reactions between O_3, O, O_2 and O_2^*. Equations with more than four constants are always obtained and, as the value of some of these constants is not known, it is easy to represent the general course of the reaction by choosing suitable values for them. It is, however, impossible to find an equation which gives, for small concentrations of ozone ($\leqq$ 0.5%) and high oxygen pressures, a constant quantum yield and also describes the course of the reaction. Warburg found for ozone concentrations between 0.2 and 0.5% a constant quantum yield of 0.28; at higher concentrations, however, the velocity depends greatly on the ozone concentration and even for $O_3 \sim 0.75\%$ a quantum yield of 0.48 is obtained. This sudden transition to a zero order reaction is highly improbable. Furthermore, his results do not agree with those obtained by Regener and v. Bahr, who found a dependence of the velocity on the ozone concentration even in very dilute ozone mixtures. In the experiments of Warburg, as he himself states, there was always present an uncontrollable dark reaction which, with the long exposure necessary for a measurable amount of reaction to take place at low pressures, would be sufficiently large to obscure any expected small change in the quantum yield. It would, however, be very desirable to have these experiments repeated.

If the observation that water vapor accelerates the decomposition is correct, it can be accounted for by the reaction of excited oxygen atoms with water vapor.

In conclusion it may be said that the decomposition of ozone in the ultraviolet, as well as the influence of foreign gases and total pressure, can be explained if the primary reaction is assumed to be a dissociation into an excited oxygen atom and an oxygen molecule. It must, however, be emphasized that further experiments in this region would be of great use in order to elucidate the details of chain formation.

The author is greatly indebted to Dr. G. B. Kistiakowsky for permission to use his unpublished experiments. Thanks are also due Dr. O. R. Wulf of Washington, who kindly communicated the results of his investigations of the spectrum of ozone, and Dr. E. O. Wiig for translating the paper into English.

Summary

1. A critical survey of the experimental data involving the photochemical decomposition of ozone has been given.
2. The kinetics of the reaction have been explained on the assumption that the ozone spectrum shows predissociation and that the primary process is therefore $O_3 + h\nu \longrightarrow O_2 + O$. In red light a normal oxygen atom is assumed to be formed and in the ultraviolet an excited atom.
3. The probability of the occurrence of the reaction $O + O_3 \longrightarrow 2O_2$ has been calculated to be 5×10^{-4} if the oxygen atom is normal and it is assumed that the reaction $O + O_2 \longrightarrow O_3$ occurs only in a three-body collision.
4. The influence of temperature and of foreign gases has been discussed. The effect of gases which do not react with ozone can be interpreted by their specific influence on the three-body reaction $O + O_2 + M \longrightarrow O_3 + M$.

PRINCETON, NEW JERSEY

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF MICHIGAN]

PREPARATION AND PROPERTIES OF LEAD PERCHLORATE

BY H. H. WILLARD AND J. L. KASSNER[1]

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Introduction

Lead perchlorate was first prepared by Serullas[2] by heating lead oxide with perchloric acid. It was also prepared by Marignac[3] and Roscoe[4] by adding lead carbonate to perchloric acid and evaporating to a sirupy liquid. Roscoe was the first to point out the fact that lead perchlorate is extremely deliquescent. The formula of the salt which he obtained was $Pb(ClO_4)_2\cdot$-

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[1] From a dissertation submitted by J. L. Kassner to the Graduate School of the University of Michigan in partial fulfilment of the requirements for the degree of Doctor of Philosophy in Chemistry.

[2] Serullas, *Ann. chim. phys.*, **46**, 297 (1831).

[3] Marignac, "Oeuvres Complètes," Vol. I. p. 401 (1840–60); *Compt. rend.*, **42**, 288 (1856); *Mem. Soc. Phys. Genève*, **14**, 260 (1855); *Arch. Phys. Nat.*, **31**, 170 (1856).

[4] Roscoe, *Proc. Roy. Soc.* (London), **11**, 493 (1861); *Ann.*, **121**, 346 (1862); *J. Chem. Soc.*, **16**, 82 (1863).