[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, ILLINOIS INSTITUTE OF TECHNOLOGY]

The Decomposition of Ozone in Aqueous Solution[1,2]

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The rate of decomposition of ozone in aqueous perchloric acid has been measured spectrophotometrically, iodometrically and manometrically, and found proportional to the three-halves power of the ozone concentration, in agreement with the reaction scheme proposed by J. Weiss. In connection with the kinetic experiments, the molar extinction coefficient of ozone at 260 mμ, and the Henry's law constant, have been determined for solutions of ozone in 0.01 *M* $HClO_4$. As in the case of hydrogen peroxide, it is difficult to obtain reproducible rates of decomposition from day to day, and the greater proclivity of ozone to explosion during purification makes the problem more troublesome.

In carbon tetrachloride,[3] and in aqueous acid solution,[4,5] the absorption spectrum of ozone is closely similar to that of gaseous ozone.[6] Weiss[4] found, however, that in increasingly alkaline solutions of ozone in water, absorption in the ultraviolet decreases, finally disappearing in strongly alkaline medium, at −40°. On the basis of this observation, and the fact that decomposition increases rapidly with increasing alkalinity, Weiss proposed the scheme

$$O_3 + OH^- \longrightarrow O_2^- + HO_2 \qquad (1)$$

$$O_3 + HO_2 \longrightarrow 2O_2 + OH \qquad (2)$$

$$O_3 + OH \longrightarrow O_2 + HO_2 \qquad (3)$$

$$2HO_2 \longrightarrow O_3 + H_2O \qquad (4)$$

$$HO_2 + OH \longrightarrow O_2 + H_2O \qquad (5)$$

From this he obtained

$$-d[O_3]/dt = 2k_4(2k_1/k_3)^{1/2}[O_3]^{3/2}[OH^-]^{1/2} \qquad (6a)$$

if 5 is not involved, and

$$-d[O_3]/dt = (2/3)k_1[O_3][OH^-] + 2(k_1k_2k_4/k_5)^{1/2}[O_3]^{3/2}[OH^-]^{1/2} \qquad (6b)$$

if 5 is involved as well as 4; at low values of $[OH^-]$, the first term in 6b would be negligible compared to the second. Weiss recalculated some of the experiments of Rothmund and Burgstaller,[7] carried out in dilute H_2SO_4, and of Sennewald,[8] carried out in phosphate buffer solution at *p*H 5–6, and showed that in them $-d[O_3]/dt$ is certainly as nearly proportional to $[O_3]^{3/2}$ as to $[O_3]$ or $[O_3]^2$. Rothmund and Burgstaller, and Sennewald, followed the reaction iodometrically; Alder and Hill,[5] who measured the rate of decomposition in dilute $HClO_4$, followed it spectrophotometrically and iodometrically. Alder and Hill found the rate proportional to $[O_3]$, but dependent upon the method of following the reaction.

In all cases the reproducibility of the experiments was rather poor; this was attributed by Rothmund and Burgstaller to the presence of unidentified impurities. The present study was undertaken on the assumptions that ozone was not unlike hydrogen peroxide, in that pure material, in properly conditioned containers or in solutions free from metal ions, and reactive organic substances, might be quite stable, and that further kinetic studies might help to elucidate the decomposition. Three methods of following the decomposition were used in the present study—iodometric, spectrophotometric and manometric.

Experimental

Spectrophotometers.—These were a Beckman DU and a Cary Recording Quartz Spectrophotometer, the latter having a program attachment. The absorption cells were of silica, cylindrical in shape, with a light path of 1 cm., and capacity of 3–5 ml. During operation the cells were thermostated at 24.9 ± 0.05°.

Materials Other Than Ozone.—The water was triply distilled. Laboratory distilled water was heated with $KMnO_4$ and NaOH and distilled into the pot of a quartz still in which the third distillation was made; during this, the flow of cooling water was reduced to permit only partial condensation of vapors.

Perchloric acid solutions were prepared from Baker 72% $HClO_4$, phosphoric acid solutions from Baker and Adamson 85% H_3PO_4, reagent grade. Glycine, K_2SO_4, KH_2PO_4 and Na_2HPO_4 were C.P. chemicals recrystallized by us several times from triply distilled water. Other chemicals were of C.P. or reagent grade.

In the earlier experiments stopcocks were lubricated with Halocarbon grease; in the later ones, with a mixture of polyperfluorovinyl chloride and colloidal silica of the desired viscosity.[9]

Ozone.—The starting material was either a 70–30 liquid mixture of ozone and oxygen,[10] or liquid ozone saturated with oxygen,[11] supplied by the Armour Research Foundation. The latter contained less than 1% of oxygen.

Preparation of Ozone Solutions.—In the early part of the work the starting material was the ozone–oxygen mixture, and from 2 to 6 distillations were carried out, in apparatus of the conventional vacuum-line type, to purify the ozone. Several explosions occurred during this period, and partly as a result of the recurring destruction of the apparatus, and partly owing to the fact that liquid ozone containing less than 1% of dissolved oxygen had become available to us, we decided to simplify the handling of the ozone and the preparation of the solutions as much as possible.

Figure 1 is a schematic diagram of the set-up finally adopted (apparatus V). In the diagram, T is the ozone transport tube; F the saturator, of 1000-ml. capacity; G a magnetic stirrer; J a differential manometer filled with 0.01 *M* $HClO_4$ and used as a null instrument; K a mercury-filled manometer; D a trap packed with pieces of Pyrex rod and tubing; C a trap packed with glass wool, and B a trap containing KI solution. Inside F there was a magnet (not shown) encased in glass, Teflon, or Kel-F. Liquid (usually 500 ml.) was introduced into F through M, which was then sealed off. The box L, which rides on one arm of J, could be filled with Dry Ice, to seal the manometer; similarly, the outlet tube of the saturator could be sealed by packing H in Dry Ice, and in operation H was kept frozen except when samples were withdrawn from the saturator;

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[1] Presented at the sixteenth midwest regional meeting of the American Chemical Society, Omaha, Nebraska, November, 1954.

[2] Abstracted in part from the M.S. Thesis of Claude C. Herrick, Illinois Institute of Technology, January, 1955.

[3] G. W. Robinson, M.S. Thesis, Georgia Institute of Technology, 1949.

[4] J. Weiss, *Trans. Faraday Soc.*, **31**, 668 (1935).

[5] (a) M. G. Alder and O. R. Hill, THIS JOURNAL, **72**, 1884 (1950); (b) M. G. Alder, Ph.D. Thesis, The University of Utah, 1950.

[6] A. Lauchli, *Z. Physik*, **53**, 92 (1929).

[7] V. Rothmund and A. Burgstaller, *Monatsh.*, **34**, 655 (1913).

[8] K. Sennewald, *Z. physik. Chem.*, *A* **164**, 305 (1933).

[9] (a) A. C. Jenkins and C. M. Birdsall, *J. Chem. Phys.*, **20**, 1158 (1952); (b) Fluorolube L. O. from the Hooker Electrochemical Co., Niagara Falls, N. Y., and Santocel C from the Monsanto Chemical Co., St. Louis, Mo.

[10] H. J. Schumacher, *ibid.*, **21**, 1610 (1953).

[11] C. Brown and K. D. Fransom, *ibid.*, **21**, 917 (1953).

this was necessary because stopcock 3 was not greased (prior to apparatus V, the stopcock corresponding to 3 had been greased). Water from a constant-temperature reservoir was pumped through the cylindrical Plexiglass tank E, in which the temperature was constant to ±0.1°. In front of the apparatus there was a shield of safety-glass which could be slid back and forth on a trolley, and attached to the shield there was a lever for turning stopcocks. Explosions occurred on two occasions in apparatus V.

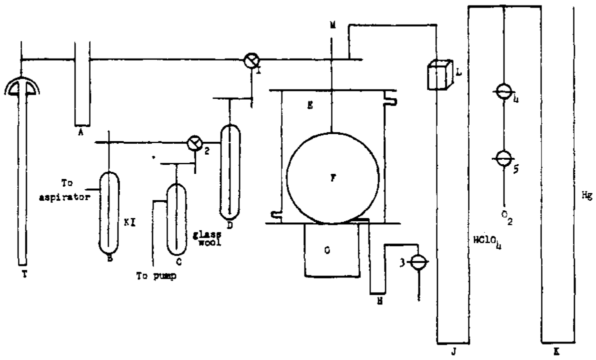

Fig. 1.—Apparatus V for handling ozone.

The procedure after the introduction of liquid into F was as follows. With T cooled in liquid oxygen and C and D in liquid nitrogen, the system to the left of cock 1 was evacuated, and pumping continued for several hours. Then, with H and J sealed, the system to the right of cock 1 was outgassed. Next a Dry Ice-bath was placed around A and one of CS_2 slush (−112°) was substituted for the liquid oxygen bath around T, bringing T to the boiling point of ozone.[9a] The gases now present to the left of cock 1 were released by a quick turn of the cock, and condensed in D; after this, 1 was turned to connect T to F and evaporation of ozone into F was allowed to go on for 30 minutes. At the end of the 30-minute period the Dry Ice was removed from L, the CS_2 bath around T was lowered, and the pressure in F allowed to build up to 1000 mm., whereupon cock 1 was turned so as to condense the remaining ozone in D. From D the excess ozone was drawn with the aid of the aspirator into the KI solution in B. When the excess ozone had been destroyed, the magnetic stirrer was turned on and the pressure in F first fell as the ozone dissolved, and then rose owing to its decomposition.

The Iodometric Analysis for Ozone.—For the iodometric analysis we used three methods, which will be referred to as the direct, the indirect, and the aeration.

In the direct method 25–50 ml. of water, 5 ml. of 4% KI and 2 ml. of starch solution were put into a 125-ml. glass-stoppered flask containing a small Teflon-encased magnet as stirrer. The flask was weighed, 10–25 ml. of 0.01 *N* $Na_2S_2O_3$ was introduced, and the flask was weighed again, after which the ozone solution was run in from the saturator, or from a siphon attached to a sampling tube, until the blue color lasted 30 seconds.[12] Care was taken that the tip of the inlet tube should always be beneath the surface of the solution in the flask during the introduction of the ozone solution.

In the indirect method the ozone solution was run into a weighed flask containing KI solution, the flask was reweighed, and the solution acidified and titrated with thiosulfate. If the *p*H of the ozone solution was below 3, sufficient Na_2HPO_4 to neutralize the acid was added to the KI solution, and after liberation of iodine the solution was acidified and titrated with thiosulfate.[13] In the case of the kinetic experiments carried out in the presence of arsenate buffers, the titration was made with standard arsenite.

In principle, the aeration method consists of sweeping the ozone from its solution by a stream of inert gas, and carrying it into neutral KI solution, where one mole of I_2 should be liberated per mole O_3.[14] Ozone solution (20–50 ml.) was run from the saturator into a calibrated sampling tube, filling the tube to overflowing; then a cap with an attached plunger was put on the sampling tube, squeezing out the upper layer of solution and bringing its volume to the calibrated figure. The cap was removed, the tube attached to the bubbling towers on the aspirator line, and for 10 minutes nitrogen was drawn through the ozone solution, then through 4% KI.

The results obtained by the direct and indirect methods were in good agreement for ozone solutions more dilute than 3×10^{-3} *M*, and their consistency was better with the direct method. The direct method was found, however, to be in disagreement with the indirect, and the discrepancy to increase rapidly with $[O_3]$, for $[O_3] > 3 \times 10^{-3}$ *M*. Measurement of the oxygen evolved upon complete decomposition of the ozone in a sample of the solution showed the direct method to be in error; there is here, apparently, interference from a reaction between ozone and thiosulfate. With the aeration method, our results were poorly reproducible. To cite a typical case, three samples of a solution of ozone in 0.01 *M* $HClO_4$, at 0°, were withdrawn from the saturator in rapid succession and gave $[O_3] = 8.7$, 7.0 and 7.6×10^{-3} *M*, respectively, upon analysis by the aeration method.

The Spectrophotometric Analysis.—The ultraviolet absorption spectrum of ozone in 0.01 *M* $HClO_4$, at $[O_3] = 6.72 \times 10^{-4}$ *M*, was determined with the Cary spectrophotometer, and the maximum found to lie at 260 mμ, as reported by Alder and Hill.[5] The extinction coefficient at 260 mμ was then determined as described below.

A 100-ml. volumetric flask was filled with 12 *N* HNO_3 and heated at 100° for an hour, cooled, emptied and rinsed thoroughly with redistilled water. Into the flask was run, from the saturator, a convenient volume of the solution of ozone in 0.01 *M* $HClO_4$, and this was diluted with a solution of 0.01 *M* $HClO_4$ which had previously been saturated with ozone, then freed of ozone by heating at 60° for 15 minutes. A sampling tube was filled with solution from the flask, and the siphon attached; the absorption cell was rinsed four times with solution from the tube, then the cell was filled, and the optical density measured. As quickly as possible thereafter the solution in the tube was analyzed by the direct method. Next, the cell was emptied, refilled, and a second measurement of the optical density made. The two measurements were in most cases the same; if not, their average was used.

The solutions examined, which were $(0.5 \text{ to } 7) \times 10^{-5}$ *M* in ozone, and 0.01 *M* in $HClO_4$, exhibited conformity to Beer's law, the extinction coefficient being 2930 ± 32 l./mole cm. at λ 260 mμ. The extinction coefficient at other wave lengths was obtained from the absorption spectrum of the 6.72×10^{-4} *M* solution mentioned above, and is shown in Fig. 2, together with that of gaseous ozone, calculated from the data of Lauchli.[6]

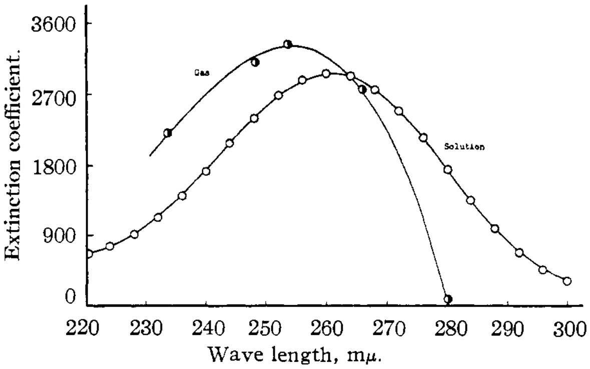

Fig. 2.—The extinction coefficient of ozone in the gas phase and in 0.01 *M* $HClO_4$ solution.

The Solubility of Ozone in 0.01 M $HClO_4$.—In the kinetic experiments followed by change of pressure, it was necessary to know the ozone concentration in terms of its partial pressure, and in order to determine the Henry's law constant experiments were carried out as follows.

After the saturated solution had been prepared in F, and the pressure had risen by *ca.* 50 mm. above the minimum

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[12] F. O. Rice, M. Kilpatrick and W. Lemkin, THIS JOURNAL, **45**, 1361 (1923).

[13] E. D. Boelter, G. L. Putnam and E. I. Lash, *Anal. Chem.*, **22**, 1533 (1950).

[14] *Cf., e.g.*, L. R. B. Yeatts, Jr., and H. Taube, THIS JOURNAL, **71**, 4100 (1949).

value (*cf.* "Preparation of Ozone Solutions") the pressure was read and two portions of the liquid were run out and analyzed by the indirect method. Since the liquid in H would not have been in equilibrium with the gas, only the second portion was used to obtain the concentration of the liquid phase. The reading of the pressure, and withdrawal of samples, was repeated at intervals over a period of 24–48 hours.

Had there been no change in volume of the liquid and gas phases, the ozone pressure at time t (assuming the solubility of oxygen to be negligible) would be given by the equation

$$P_{O_3} = 2\{P^{\infty} - P - {}_1P_{O_2}\} \tag{7}$$

where P is the total pressure at time t, P^{∞} that after complete decomposition, and ${}_1P_{O_2}$ the pressure of the oxygen which would be formed from the ozone present in the liquid at time t. However, the final pressure reading was taken before decomposition was complete, and owing to sampling there were changes in volume, and loss of ozone from the system. Let $\bar{P}^t$ represent the final pressure, read at t^t; let V represent the volume of the gas phase at time t, and V^t that at time t^t; and let $(n_{O_3})_r$ represent the number of moles of ozone removed by sampling between times t and t^t. Then substituting for P^{∞} in (7) the approximate value P^t

$$P^t = V^t(\bar{P}^t - P_{H_2O})/V + P_{H_2O} + P_r \tag{8}$$

where

$$P_r = 1.5(n_{O_3})_r\,RT/V \tag{9}$$

there is found a first value of P_{O_3}. The first value of P_{O_3}, plotted *vs.* $[O_3]$, gave a line with a negative intercept on the axis of pressure, owing to the fact that decomposition was not complete at time t^t. Increments were then added to $\bar{P}^t$ until the resulting line passed through the origin, and the slope of this line was taken as the Henry's law constant $K_{O_3} = P_{O_3}/[O_3]$ (*cf.* Table I). When the solubility of oxygen was taken equal to the solubility in water, and P and P^t were corrected accordingly, the change did not affect the second significant figure in K_{O_3}. Attempts were made to estimate the ozone remaining at t^t by running out and analyzing the liquid, and by drawing the gas through KI solution in two bubbling towers; copious white smoke (probably I_2O_5) appeared in the towers, however, and the results were considered unreliable.

TABLE I

$K_{O_3} \times 10^{-4}$ (MM. AT 0°)(MOLE/L.)$^{-1}$

Temp., °C.	Solvent 0.01 *M* $HClO_4$	H_2O	3.5% NaCl	0.1 *N* H_2SO_4
10		4.4[a]		
15.2	5.4[b]			
19		5.2[c]		
20	6.8[b]	5.3,[d,e] 5.8[a]	10[d,e]	6.5,[a] 7.9[f]
25	7.6[b]			
30	8.4[b,g]	8.5[a]		

[a] B. Kawamura, *J. Chem. Soc.*, (*Japan*), 53, 783 (1932). [b] Present investigation. [c] V. Mailfert, *Compt. rend.*, 119, 951 (1894). [d] E. Briner and E. Perrottet, *Helv. Chim. Acta*, 22, 397 (1939). [e] At 19.8°. [f] R. Luther, *Z. Elektrochem.*, 11, 832 (1905). [g] At 29.4°.

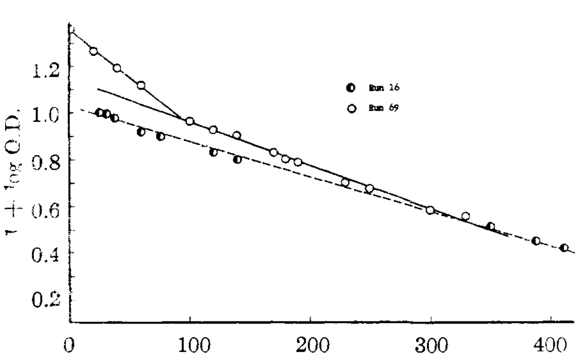

Fig. 3.—Effect of initial ozone concentration.

The Procedure for the Kinetic Experiments.—The spectrophotometric experiments were carried out in the silica absorption cells and, since liquid was forced out, and a bubble formed, as the ozone decomposed, the cell was placed in the holder with the stopper down so as to make a liquid seal and prevent loss of gaseous ozone. Tests made to see if there was an effect of the beam of light upon the rate of decomposition showed no significant difference in rate between much-exposed and little-exposed solutions.

The iodometric experiments were carried out in glass-stoppered flasks or in sampling tubes, one flask or tube being used for each determination of concentration.

The manometric experiments were carried out in the saturator of apparatus V. The ozone concentration in the liquid phase was obtained from the pressure readings in the following way. Let

a = moles O_3 introduced into saturator
x = moles O_3 decomposed by time t
$[O_3]$ = moles O_3 per l. soln. at time t
V_g = vol. of gas, V_1 = vol. of soln., in l.
K_{O_2} = Henry's law constant for oxygen, K_{O_3}, for ozone

Then assuming equilibrium between gas and liquid

$$P_{O_2} = (RT/V_g)(1.5x)/\{1 + (RT/V_g)(V_1/K_{O_2})\}$$

$$P_{O_3} = (RT/V_g)(a - x)/\{1 + (RT/V_g)(V_1/K_{O_3})\} = (RT/V_g)(a - x)/C$$

$$(a - x) = [O_3]\,V_1C/(C - 1)$$

and

$$P^{\infty} - P = [O_3]\,V_1(1.5B - A)C/AB(C - 1) = K'[O_3] \tag{10}$$

where

$$A = V_g/RT + V_1/K_{O_2};\ B = V_g/RT + V_1/K_{O_3}$$

In calculating K', K_{O_2} was taken from the solubility of oxygen in water; the exact value of K_{O_2} was not important be-because the first term in A was *ca.* 40 times as large as the second.

The value of P^{∞} was obtained either by waiting until there was no change in P over a period of several hours, or by aspirating the gases through KI solution after the last pressure reading. The analysis for the residual ozone was made in this way in order to permit the use of the same 500 ml. of $HClO_4$ solution in several runs. Assuming the residual ozone to correspond to 50 mm. in oxygen pressure, and assuming the error in the analysis by the aeration method to be ±10%, the resulting error in k at 50% decomposition would be ±2% and at 87% decomposition ±6% if $P^{\infty} - P_0 = 500$ mm.

The Kinetic Results

In 0.01 *M* $HClO_4$ Solution.—The early kinetic experiments were carried out with $[O_3]_0$ *ca.* 3×10^{-4} *M*, the reaction being followed spectrophotometrically and in some cases iodometrically also. Alder and Hill[5] had reported that in $HClO_4$ solution the decomposition of ozone follows the first-order law, and the dashed line of Fig. 3, which represents one of our early spectrophotometric experiments, shows that for one half-life we found fair conformity to that law. We also found the iodometric specific rate to be about the same as the spectrophotometric.

When more concentrated solutions of ozone were prepared, however, it became apparent that the tendency of the first few measurements to lie above the line, on the plot of log O.D. *vs.* time, was real; *cf.* the upper curve in Fig. 3, which is typical. We next examined the fit of the kinetic data to the equations[7,8]

$$-d[O_3]/dt = k_2[O_3]^2$$

and

$$-d[O_3]/dt = k_1[O_3] + k_2[O_3]^2$$

but for both k_2 exhibited a trend within a given experiment. It was found that when log [d(O.D.)/d*t*] was plotted *vs.* log O.D., the points, though sometimes scattered, indicated that the kinetic equation, as suggested by Weiss,[4] was

$$-d[O_3]/dt = k[O_3]^{3/2} \quad (11a)$$

or in integrated form

$$2\{1/[O_3]^{1/2} - 1/[O_3]_0^{1/2}\} = kt \quad (11b)$$

Figure 4 shows the conformity to the three-halves-order law found in a typical experiment in which iodometric and spectrophotometric measurements were made on portions of the same solution. The spectrophotometric readings in Fig. 4 start later than the iodometric because the initial absorption was too great to measure. Figure 5 shows the conformity to the three-halves-order law found in three manometric experiments carried out by admitting ozone to the same charge of 0.01 M HClO₄ in the saturator of apparatus V.

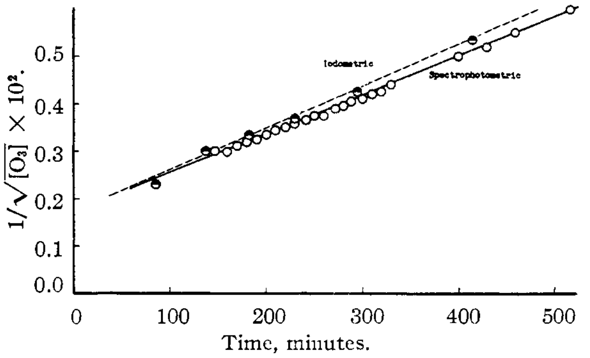

Fig. 4.—Comparison of spectrophotometric and iodometric data for run 49.

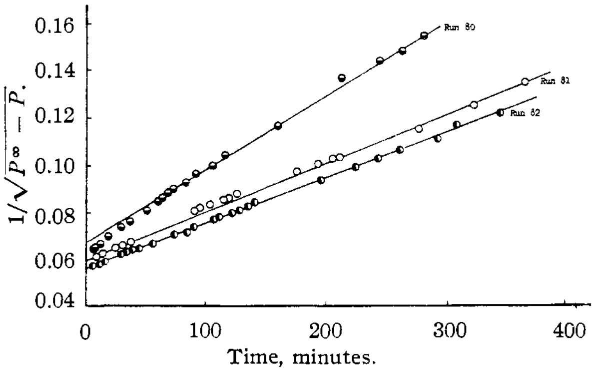

Fig. 5.—Test of three-halves-order law.

For experiments carried out over a period of 18 months with ozone solutions prepared in app. I, II and III k_{sp} was found to be 0.15 ± 0.04, k_{iodo} to be 0.15 ± 0.05 (mole/l.)$^{-1/2}$ min^{-1}. With the installation of app. IV and V the reproducibility of k_{sp} became poor. Although the spectroscopically-measured decomposition followed the three-halves-order law except in a few erratic runs, k_{sp} ranged from 0.15 to 1.5. It is not known to what this was due. However, the manometric experiments, which were carried out in app. V only, were in reasonable agreement with the earlier values of k_{sp}, and k_{iodo}, although in runs carried out consecutively with the same HClO₄ solution kept in the saturator there was a tendency toward decrease in rate with use (*cf.* runs 80, 81 and 82 in Fig. 5, for which k_{man} = 0.15, 0.10 and 0.09, respectively).

These observations suggested that the experiments were being affected by impurities. The following experiments were carried out using a Kel-F-encased magnet, and with stopcocks 1 and 2 lubricated with a viscous Fluorolube–Santocel mixture; there was no noticeable greasiness in the saturator. Although it had been observed that bulbs filled with ozone gas retained their blue color for many days, tests were first run to see if there was an effect of the diffuse light of the laboratory on the rate of decomposition of dissolved ozone. Figure 6 shows a manometric experiment in which the tank E in Fig. 1 was covered initially with a photographer's cloth; Fig. 7, an experiment in which the cloth was put on after 100 minutes. The increase in rate upon removal of the cloth is very sharp, in Fig. 6; in Fig. 7, no great immediate change in rate occurs when the cloth is put on, but the decrease becomes evident 50–100 minutes later. This pair of experiments was repeated, with similar results; then a set of four runs was carried out in the dark at 25° using the same HClO₄ solution (which had already been used in two dark-and-light runs), and k_{man} found for the set to be 0.021 ± 0.003 (mole/l.)$^{-1/2}$ min.$^{-1}$, with no trend.

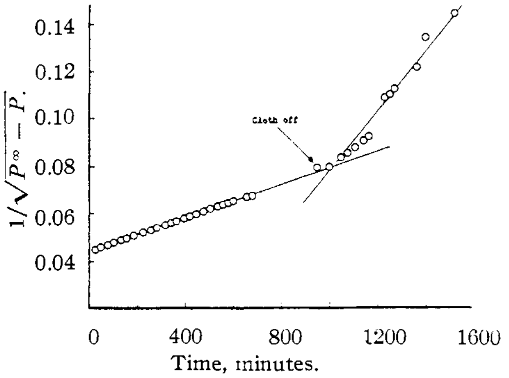

Fig. 6.—Effect of light I: Exp. 89 at 15°.

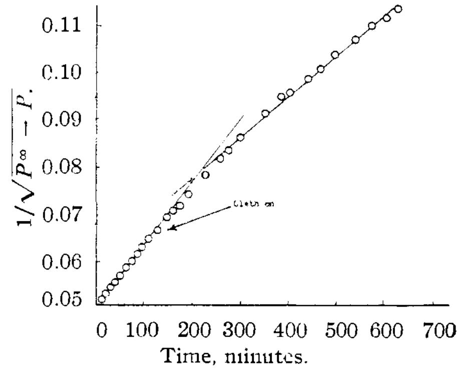

Fig. 7.—Effect of light II: Exp. 87 at 25°.

To test the effect of impurities, we carried out three manometric experiments in the dark at 25°, the added substance being present at a concentration of 0.001 M in each case. The times required for $P^\infty - P$ to reach $3(P^\infty - P_0)/4$ were

Added substance	Quarter-life, min. Calcd.	Quarter-life, min. Obsd.
$Cu(ClO_4)_2$	178	22
$Fe(ClO_4)_3$	138	5000
Glycine	203	10

The calculated quarter-life was obtained from $k = 0.021$ and the experimental $P^\infty - P_0$, *i.e.*, it is the quarter-life expected in pure 0.01 *M* $HClO_4$. With $Cu(ClO_4)_2$, and with glycine, there was deviation from the three-halves-order law; with $Fe(ClO_4)_3$ the decomposition was so slow that *ca.* three-quarters of the ozone still remained after 4 days. There was probably some oxidation of glycine.

In Solutions of Various Acid Concentrations.—The experiments now to be discussed were carried out before the manometric experiments described above; had experiments been carried out in the dark on solutions conditioned by repeated use, a lower rate of decomposition would probably have been found. The experiments should, however, give the magnitude of the effect caused by change in hydrogen ion concentration.

Unless otherwise stated, the solutions of Table II were prepared by passing ozone into the acid solution in the saturator of apparatus I, and $[O_3]_0 \simeq 3 \times 10^{-4}$ *M*.

TABLE II

THE EFFECT OF ACID CONCENTRATION ON THE DECOMPOSITION OF OZONE AT 25°

$HClO_4$, *M*	*k* in (moles/l.)$^{-1/2}$ min.$^{-1}$ Spectrophotometric	Iodometric
0.961	0.60	
.100	.50	
.0100	.17	0.22[a]
	.15 ± 0.04[b]	.15 ± 0.05[b]
.0010	.28	.26[a]
1×10^{-4}	.42	.44[a]
2.5×10^{-5}	1.2	
1×10^{-5}	1.9	1.9[a]

[a] From smoothed curve. [b] Average for solutions prepared in app. I, II and III; $[O_3]_0 \leqq 3 \times 10^{-3}$ *M*.

Experiments were also carried out in the solutions

$HClO_4$, 0.01 M; H_3BO_3, 8×10^{-4} *M*
H_2SO_4, 0.01 M
H_2SO_4, 0.001 M; $HClO_4$, 0.02 M
CF_3COOH, 0.001 M

and the results were about the same as those given in Table II.

In NaOH Solution.—The NaOH solutions were prepared by dilution of carbonate-free 0.1 *M* NaOH with CO_2-free water, then ozone was passed into the dilute caustic in the saturator of apparatus I.

The rate of decomposition was found proportional to $[O_3]^2$. Plots of $[O_3]^{-1/2}$ *vs.* time were curves concave downward in all cases, showing the failure of the three-halves-order law. In spite of the uncertainty in $[OH^-]$, and (owing to the speed of the reaction) in the iodometric determinations, the results below show that the rate increases as $[OH^-]$ increases

NaOH, *M*	k_2 in (moles/l.)$^{-1}$ min.$^{-1}$, at 25° Spec.	Iodo.
10^{-4}	1800	740
10^{-5}	360	290
10^{-6}	100	220

In Phosphate and in Arsenate Buffer Solutions at 25°.—Three sets of experiments were carried out. In the first, ozone was passed into 1/1 buffer solutions made from KH_2PO_4 and Na_2HPO_4, with K_2SO_4 added to bring the ionic strength to 0.5. The *p*H before entrance of ozone was 6.8, and the concentration of the buffer constituents ranged from 0.001 to 0.025 *M*. Preliminary tests had shown that during a 30-minute saturation in apparatus I the *p*H fell by a unit or more in buffers as dilute as 0.001 *M* and by a small amount in buffers as concentrated as 0.01 *M*, and that the low *p*H persisted for a long time, and so appeared unconnected with the decomposition of ozone. The results of the kinetic runs (all spectrophotometric) are shown in Fig. 8; in runs 1 and 2, the solutions were 0.001 *M* in the buffer constituents; in run 8, 0.01 *M;* and in runs 3 and 4, 0.025 *M*. The conformity to the three-halves-order law is shown in runs 3 and 8, where the decomposition was followed to over 90 and 80%, respectively, of completion. For the set, $k_{sp.} = 1.2 \pm 0.6$ (mole/l.)$^{-1/2}$ min.$^{-1}$. The slower rate of decomposition in runs 1 and 2 was probably due, in part at least, to a lower *p*H, and the faster rate in run 8, which had a saturation period of two minutes only, to a higher *p*H.

The second set was carried out in 1/1 H_3PO_4–NaH_2PO_4 buffer solutions to which no solvent salt was added. When the solutions were made up individually from standard NaOH and H_3PO_4 solutions there was more erraticalness in the kinetic data than when they were made up by dilution of a stock buffer. Even in the latter case the data in a given run were less consistent than in, *e.g.*, run 3 or 8 of Fig. 8; however, the fit of the data to the three-halves-order law was better than to the others. In the four experiments in which the phosphate solutions were prepared by dilution of a stock buffer, the concentration of buffer constituents ranged from 0.025 to 0.10 *M*, k_{sp} was found to be 0.30 ± 0.08, $k_{iodo.}$ 0.20 ± 0.04; there was no discernible effect of buffer concentration. The rate in these buffers was thus about the same as in a perchloric acid solution of the same *p*H.

In the third set the decomposition was measured in 1/1 H_3AsO_4–NaH_2AsO_4 buffer solutions prepared by dilution of a stock solution of *p*H 2.3. No solvent salt was added. The concentration of each buffer constituent ranged from 0.005 to 0.10 *M*. As with the second set of phosphate buffers there was some erraticalness in the kinetic data, and in addition the variations in *k* from run to run were large; the average of the four spectrophotometric and two iodometric *k*'s is 1.4 ± 0.8, which is appreciably higher than *k* for a perchloric acid solution of the same *p*H. The high value of *k*, and the erraticalness in the kinetic data, are believed due to impurities.

Discussion

The first conclusion to be drawn from the experiments described is that in aqueous perchloric acid alone the decomposition follows the three-halves-order law; the fit of the kinetic data to this law was good except in a few cases, and was much better than the fit to the first-, second-, or first-plus-second-order law. The fit to the first-order law re-

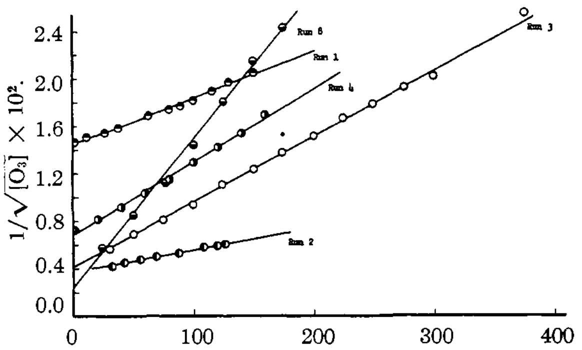

Fig. 8.—The three-halves-order law in KH_2PO_4–Na_2HPO_4 buffer solution.

ported by Alder and Hill is probably to be attributed to their use of dilute ozone solutions only, and to the fact that in many experiments the reaction was not followed very far. In Fig. 9 we have replotted the spectrophotometric data of run 1 of Alder and Hill, carried out in 10^{-2} M $HClO_4$ at 0°, according to the first-order law (scale to left), and according to the three-halves-order law (scale to right). This run, which was followed to 87% of completion,[5b] clearly conforms more closely to the latter law. To calculate $[O_3]$ for Fig. 9 we used the value of the extinction coefficient which we determined at 25°. From the slope of the line k is found to be 0.44, which is of the same order of magnitude as the velocity coefficient given in Table II for 25°.

In the experiments in buffer solution the conformity to the three-halves-order was better than to the other laws, and any departure, *e.g.*, at the end of the reaction, appeared to be random. In the phosphate buffer solutions prepared from recrystallized salts, the conformity was good in the two experiments followed nearly to completion.

In alkaline solution the experiments show definite departure from the three-halves-order law. Although the conformity of the scanty data to the second-order law must be regarded as empirical, from the change in the absorption spectrum[4] it would be expected that as $[OH^-]$ increases a point will be reached where the concentrations of species other than O_3 would no longer be negligibly small, and the conditions for which the equations 6 were derived would no longer apply.

There are some striking differences between our findings and those of Rothmund and Burgstaller: the greater rate of decomposition in 1 M than in 0.01 M $HClO_4$, as compared with their much smaller rate in 1 N than in 0.01 N H_2SO_4; the retardation in the presence of $Fe(ClO_4)_3$ as compared with their acceleration in the presence of $FeK(SO_4)_2$; the acceleration in the presence of $Cu(ClO_4)_2$ as compared with their lack of any effect of $CuSO_4$.

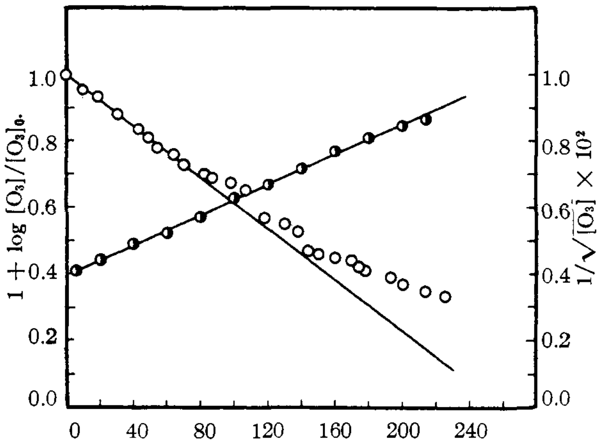

Fig. 9.—Spectrophotometric run I of Alder and Hill: O, first order (scale at left); ◑, three-halves order (scale at right).

The difficulty encountered in preparing ozone solutions which have reproducible rates of decomposition is reminiscent of the capricious behavior of hydrogen peroxide, for which Dainton and Rowbottom[15] report that they found the order of the thermal decomposition to be about 1.5, so that the reaction is unlikely to be heterogeneous. The fact that the decomposition of ozone in acid solution is of order 1.5 with respect to ozone calls to mind the gas-phase chlorine-catalyzed decomposition of ozone, as well as the gas-phase decomposition of ozone in ozone–oxygen mixtures not too rich in oxygen.[16] An investigation of the photolysis of ozone solutions, carried out with the same care as the recent studies on hydrogen peroxide,[15] seems to be in order.

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(15) For references, see F. S. Dainton and J. Rowbottom, *Trans. Faraday Soc.*, **49**, 1160 (1953).

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