mic acid vapor did not directly affect the velocity of the main reaction, tending only to mask its course in the early stages by undergoing decomposition. Nitrogen had an extreme accelerating influence on the oxidation, which could be explained by an increase in the catalytic efficiency of carbon dioxide from 14.5 to 30%, in addition to the 100% efficiency of nitrogen.

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An Anomalous Decomposition of Ozone in the Presence of Chlorine

BY LAWRENCE J. HEIDT, GEORGE B. KISTIAKOWSKY AND GEORGE S. FORBES

Several investigators[1] of the decomposition of ozone in the presence of chlorine have reported that the quantum yield, ϕ (ozone molecules decomposed per quantum absorbed), is 2.0 ± 0.2 in spectral regions where chlorine only absorbs, that the light reaction is nearly independent of the concentrations, and that the dark reaction[2] is relatively small at room temperature. The dark reaction has since been studied at 35 and 60° by Hamann and Schumacher.[3] The photolysis has been used as an actinometer.[4] The observations by Allmand and Spinks[1a] indicated that the course of the reaction was decidedly irregular. We undertook its further study at lower temperatures using an apparatus[5] recently devised for referring ϕ in gas reactions to uranyl oxalate as an actinometer. Attention is called to the stringent precautions there described regarding temperature control and pressure measurement. A second paper of Allmand and Spinks[6] stated, as we had noticed in the meantime, that the dark reaction and wall effects were important, and expressed regret that these had not been further studied. None the less, they still viewed their reaction as essentially photochemical. These workers found that with O_3 greater than 35% and Cl_2 about 1%, values of ϕ up to 59 could be obtained; these values decreased as the light intensity, I, increased, the reaction rate being approximately proportional to $I^{1/2}$; the 10° temperature coefficient of the rate under these conditions was about 1.5, as compared with 1.0 when the chlorine percentage was higher, ϕ smaller, and the rate proportional to I.

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(1) For a review of the literature see (a) Allmand and Spinks, *J. Chem. Soc.*, 1652 (1931); (b) Taylor, *J. Phys. Chem.*, **34**, 2082 (1930); (c) Schumacher and Wagner, *Z. physik. Chem.*, [B] **5**, 199 (1929); (d) Griffith and McKeown, "Photoprocesses in Gaseous and Liquid Systems," Longmans, Green and Co., New York, 1929, pp. 601–605; (e) Kassel, "Kinetics of Homogeneous Gas Reactions," The Chemical Catalog Co., Inc., New York, 1932, pp. 254–262.

(2) Bodenstein, Padelt and Schumacher, *Z. physik. Chem.*, [B] **5**, 209 (1929).

(3) Hamann and Schumacher, *ibid.*, [B] **17**, 293 (1932).

(4) Cremer, *ibid.*, **128**, 285 (1927).

(5) Forbes, Kistiakowsky and Heidt, THIS JOURNAL, **54**, 3246 (1932).

(6) Allmand and Spinks, *J. Chem. Soc.*, 599 (1932).

When high initial values of ϕ were obtained, they decreased rapidly; a similar sort of decrease is noted, under different conditions, in the present paper.

The quantum yield apparatus (Ref. 5, Fig. 2) was fused to the Pyrex train for introduction of ozone and chlorine at A (Fig. 1 of the present paper). Originally, the latter lacked the U tubes, U_1 and U_2, and greased stopcocks were present at F, G, H, *I* and J. The average quantum yields, ϕ, of thirteen preliminary experiments are noted upon the curves in Fig. 2.

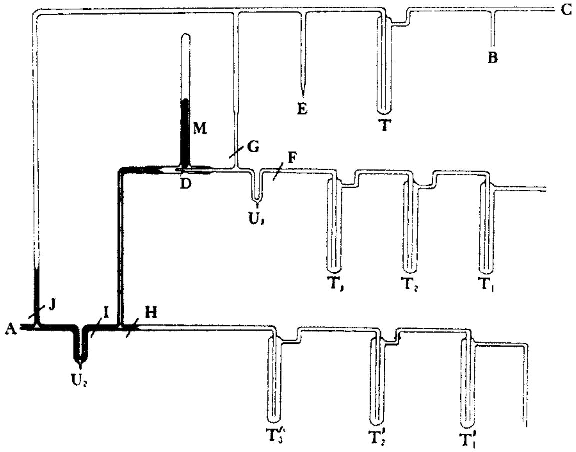

Fig. 1.

In all the figures black circles indicate darkness, open circles light absorption averaging 2.7×10^{15} quanta/sec., $\lambda = 366$ mμ, and half black circles exposure to red and yellow light. Plain circles indicate a temperature constant within 0.1° at approximately 2°, one flag 13°, two flags 25°. Whenever a new symbol appears, it defines conditions back as far as the last old symbol. Along a dotted line the temperature, θ, is indeterminate. To avoid implications regarding reaction mechanism we report only the rate of increase in total pressure, $dp/dt = m$, referred to 0° in mm. of mercury per minute. Curves representing long experiments, *e. g.*, the fourth, are broken up into sections. When a part of the experiment between sections has been omitted, the total pressure, p, at the beginning of the section is noted. Initial partial pressures are given in the accompanying tables, with $p_f - p_i$, the difference between total final and total initial pressure.

The values of ϕ in Fig. 2 are not concordant, and are in most cases smaller than 2. The irregularities seem to be independent of partial pressures of reactants. The behavior of the mixture when light and dark periods alternated, shown in the group of curves to the left in Fig. 2, differs strikingly from that observed by Allmand and Spinks[1a] in that no periods of diminishing pressure occur. Our experiments did not become consistent when the rubber grease, R, in the stopcocks was replaced by a mixture of vaseline, V, with naphthalene, N, refluxed for many hours in an atmosphere of chlorine, or by concentrated sulfuric acid, S.

Suspecting contamination of the gases or of the cell, we improved the apparatus by adding U_1 and U_2, and by eliminating all stopcocks. All parts were heated in sulfuric plus nitric acid, washed with distilled water several times after washings had become neutral, and scrupulously dried. The quartz reaction cell (Ref. 5, Fig. 2) was pumped out for several hours with a Wagner deka-micro oil pump. Air, dried with resublimed phosphorus pentoxide, was then admitted. While fusing the parts together, we blew through a sodium hydroxide tower and a trap filled with glass wool and immersed in liquid air. At B, connection was made with a McLeod gage (not shown). A two-stage mercury diffusion pump backed up by the Wagner pump was connected to the train at C through the trap, T, immersed in liquid air to intercept mercury vapor. After testing for leaks with a Tesla coil, the train was pumped out with the diffusion pump, while flaming exposed parts. Dried air was admitted through E.

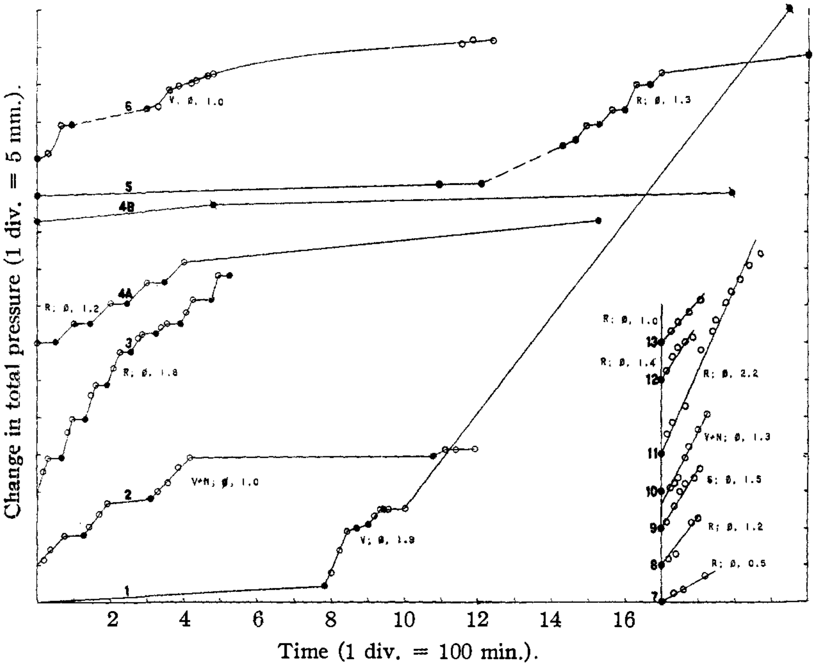

Fig. 2.

Expt.	p_{O_3}	p_{O_2}	p_{Cl_2}	$p_f - p_i$
1	300	0	60	150
5	71	96	406	36
11	55	144	494	28
13	59	64	351	30

In dim diffused light tank chlorine was fractionally distilled in a vacuum three times, occupying successively traps T_1, T_2, T_3 and the graduated tube below U_1, previously calibrated by measuring the pressure developed in the reaction vessel, C_g, by evaporation of liquid chlorine between various graduations. The chlorine was evaporated each time at −80° and the middle portion only was condensed in liquid air. Seals were made at F and G. Ozone was obtained from an apparatus lent by Professor E. P. Kohler. The electrolytic oxygen passed through sodium carbonate solution, solid potassium hydroxide, sulfuric acid and phosphorus pentoxide, in the order mentioned. The ozone was thrice fractionated much like the chlorine by suitable manipulations of a container of liquid air, the middle fractions occupying successively T_1', T_2', T_3' and the calibrated tube below U_2. A seal was then made at H. Keeping U_1 and U_2 in liquid air, the sealed capillary at D was broken by the magnetic hammer, M, and a predetermined amount of chlorine distilled into the arm of U_2 next to D. Seals were made at I and J and allowed to cool. The total volume of U_2 and connecting capillaries to the left of I and J did not exceed 2 cc. or 5% of C_g. In experiments where much chlorine and little ozone was present in U_2, the liquid air could be removed at once from U_2 so that all the ozone passed into the cell for a pressure reading while the chlorine still remained solid. After the chlorine had evaporated, the pressure was read again. If little chlorine was present in U_2, the liquid air was manipulated so that the gases distilled over together into C_g; the chlorine could then be estimated only from its liquid volume. Exposed tubes connected with C_g were wound with black tape.

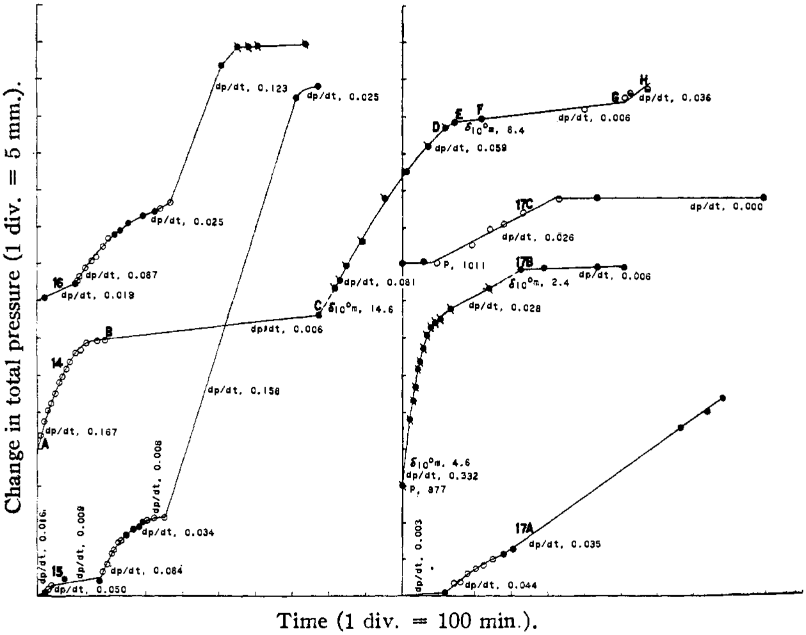

Fig. 3.

Expt.	p_{O_3}	p_{O_2}	p_{Cl_2}	$p_f - p_i$
14	147	140	374	74
15	135	133	170	68
16	132	97	300	66
17	158	130	651	79

For Experiment 14 the cell was on the diffusion pump for three hours at 25° before filling at 25°. At the start $\phi = 3$ at 2° decreasing toward B, where but a quarter of the ozone had been decomposed. The light was shut off at B. Between A and B the dark reaction was negligible. From B to C. $m = 0.006$ and no further deceleration was observed. At C, θ was raised to 13° and the ten-degree temperature coefficient, $\delta_{10°}$ m, was 14.6, a highly abnormal value suggesting the emergence of a new type of reaction, possibly a chain reaction starting on the walls. Some deceleration occurs from C to D, presumably due to a decrease in p_{O_3}. At E, θ again was lowered to 2° whereupon m from E to F was 0.006 in spite of a loss of three-quarters of the ozone remaining at C. From F to G ultraviolet light was without effect. From G to H, red light through the exit slit produced acceleration. Beyond the last recorded reading, in this and all other experiments, residual ozone was decomposed by prolonged exposure to the full light of a

Uviarc, 3 cm. from the front window. Given the final reading of total pressure, all partial pressures corresponding to any given reading of total pressure could be calculated.

Before Experiments 15 and 16, the cell was pumped out at 25° for one day with the oil pump and for a second day with the diffusion pump. Gases were introduced at 2° as in following experiments unless otherwise noted. The initial value of ϕ was 3. In each case a condition was soon attained where alternation of light and darkness had little effect upon the trend of the curves. The "fast" reaction began without elevation of temperature soon after the light was shut off. In 15, and to a considerable extent in 16, the gases became insensitive to ultraviolet light just before the fast reaction set in. Ozone undecomposed at the end of the experiments amounted to 127 and 108 mm., respectively.

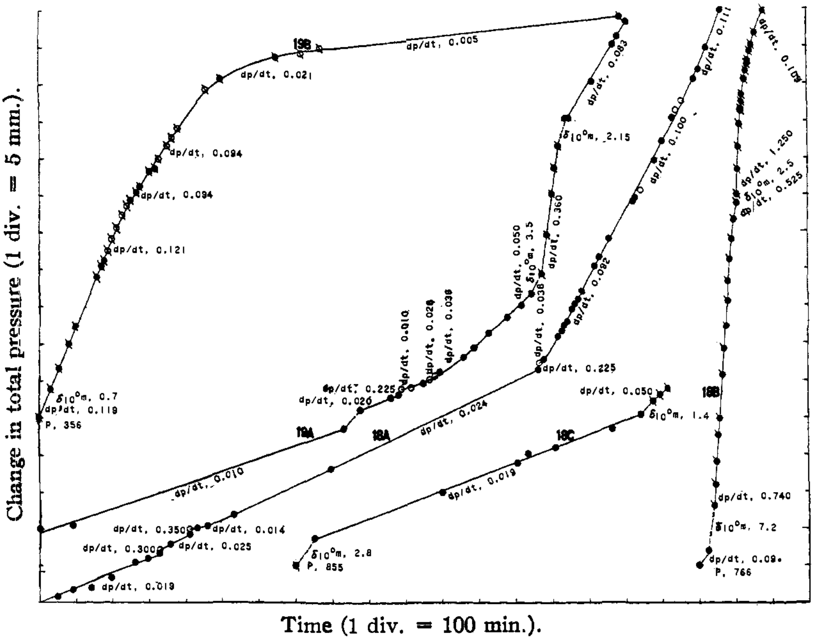

Fig. 4.

Expt.	p_{O_3}	p_{O_2}	p_{Cl_2}	$p_t - p$
18	570	32	60	285
19	457	249	105	229

Figure 2 should now be reëxamined. In Experiment 1 the cell was almost as clean as in 14, and little accumulation of impurities from stopcocks could have occurred; initial $m = 0.006$. The curve up to the intervention of the fast reaction, while somewhat terraced, is not very different from the curve in 14. Subsequent experiments 2, 3, 4, 5 and 6, between which the cell was pumped out but not otherwise cleaned, show a pronounced and persistently terraced pattern but no fast reaction occurs except possibly over a short interval in Experiment 5.

Before Experiment 17 the cell was removed from its copper thermostating jacket, cleaned as before 14 and pumped out with the oil pump while heated to dull redness. Dry air was then admitted. Although $\phi = 0.8$ (uncorrected for the dark reaction) was relatively small at the start, the slope attained after admission of light remained nearly unaltered in light and dark alike until θ was raised to 22°; $\delta_{10^\circ}\ m = 4.6$ is again large. One is tempted to connect the practical absence of the terraced pattern in the curve after light admission with the fact that the walls were cleaner than in previous experiments. After cooling, the decomposition reverted nearly to the original dark rate, m = 0.006, as against 0.003 and the system had regained its sensitiveness to light. Residual ozone was 24 mm.

Experiments 18, 19 and 20 in Figs. 4 and 5 are characterized by high initial ozone pressures. They show the impossibility of predicting the time intervening or the amount of photochemical or thermal reaction occurring before the beginning of a fast reaction. Further, they show that the fast reaction may suddenly start at any one of the temperatures used and is not dependent on a change of temperature or illumination. They also show that the fast reaction may die down and later reappear and that the induction period preceding the inception of the fast reaction decreases as experiments are started at successively higher temperatures.

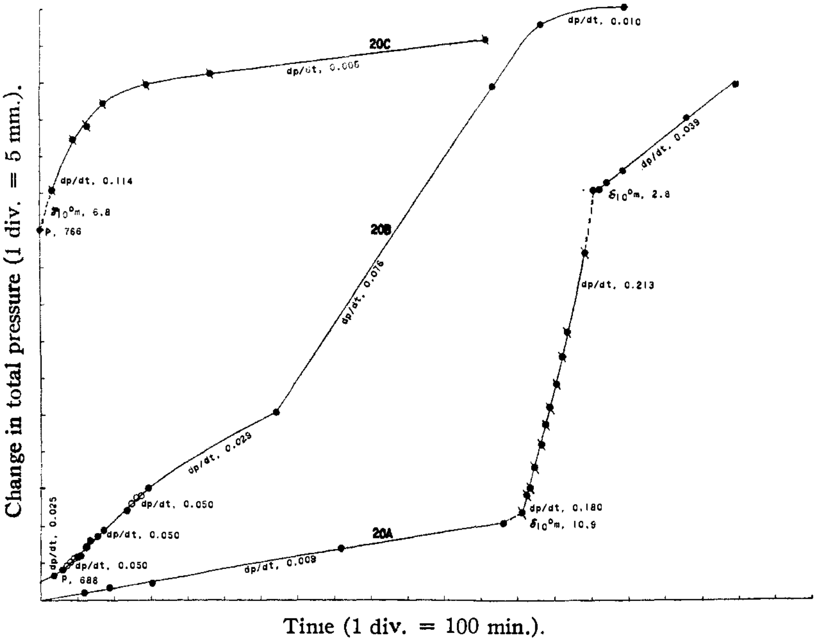

Fig. 5.

Expt.	p_{O_3}	p_{O_2}	p_{Cl_2}	$p_f - p_i$
20	406	118	90	203

Since Allmand and Spinks[1a] used a sulfuric acid manometer, Experiment 21 was carried out with 1 cc. of pure concentrated acid in the cell (wetting only a corner of C_g). The initial dark reaction at 2° was about the same as in other experiments. Upon warming to 21°, $\delta_{10°}\, m$ was 4.6, and upon cooling to 2° again, $\delta_{10°}\, m$ was 11.8. Light now accelerated the reaction moderately and the terraced pattern persisted, the reaction rate promptly decreasing when light was shut off. Again we observed no periods of decreasing pressure, such as those described by Allmand and Spinks. In the presence of sulfuric acid only we observed at 2° a white mist, formed in many of their experiments also, and found by them to contain perchloric acid. Our mists slowly disappeared on raising the temperature to 25°.

Experiment 22, a repetition of 21, agreed throughout with 21 and need not be discussed in detail.

In Experiment 23 the cell walls were entirely covered with sulfuric acid, the excess being poured out. The photochemical behavior was essentially the same as in 21 and 22, but $\delta_{10^\circ}\, m$ is smaller, indicating a further retardation of the fast reaction.

Before Experiment 24 the sulfuric acid was very carefully washed out, and 1 cc. of water was introduced. After fusing the cell to the train, the cell was pumped and filled while a block of carbon dioxide ice was held in contact with the front window to prevent evaporation of the water. At the start, at 2°, $p_{O_3} = 369$, $p_{O_2} = 125$, $p_{Cl_2} = 300$ and $m = 0.004$. Warmed to 22°, $\delta_{10^\circ}\, m = 8.25$, after which m suddenly fell off with the cell still at 22°, to a quarter of its previous value. It then suddenly trebled, and was later cut in half. In the final stages of the experiment $\delta_{10^\circ}\, m$ was 3.5 and 0.9, respectively, as the reaction progressed.

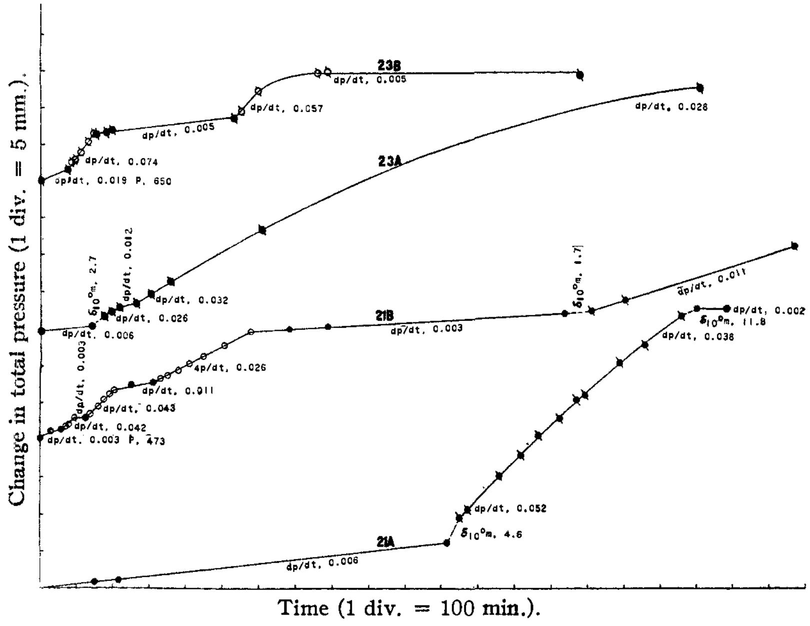

Fig. 6.

Expt.	p_{O_3}	p_{O_2}	p_{Cl_2}	$p_f - p_i$
21	194	54	185	97
23	157	356	80	79

Experiments 21 to 24 prove that variations in m (θ constant) are less striking in the presence of sulfuric acid or water, but persist even when the walls are completely covered with one of these liquids, that is, in the absence of an uncontaminated quartz surface. On the other hand, a mixture of ozone and chlorine does not become insensitive to light when the whole surface of the cell is contaminated.

In Experiment 25 ozone without chlorine was carefully investigated over two hundred hours to substantially complete decomposition, one hundred pressure readings being made. The cell had been scrupulously freed from acid, flamed and pumped for a whole day. At the start, at 2°, $p_{O_3} = 490$, $p = 623$ and $m = 1.20$. After two and one-half hours p was only 653, but m had decreased to 0.026, following a pseudo-logarithmic curve. Raised to 22°, m was not quite doubled. Exposed behind the slit to red light, m at once increased to 0.165 but fell off gradually without increase at any time to 0.012 for $p = 795$, the corresponding dark rate being 0.002. These results agree substantially with a previous investigation by one of us,[7] except for the initial rapid dark reaction above described. Kassel,[8] indeed, mentions the disagreement among previous workers in this respect. It might be urged that the fast reactions observed in the dark in the earlier stages of our experiments with chlorine present also depend upon the rapid decomposition of ozone *per se*, but the fast reactions springing up in the later stages of the experiments with chlorine find no counterpart upon the curve of pure ozone.

In Experiment 26 C_g was replaced by a 50-cc. Pyrex bulb, very carefully cleaned, and flamed while the diffusion pump was running. The bulb was filled at 23° and the reaction studied only in the dark at 23, 35 and 50° with the usual precautions. From $p_{O_2} = 518$, $p_{Cl_2} = 70$ and $p = 652$ to $p = 705$ at 23.2°, m changed from 0.476 to 0.435. At 35.2° for $p = 740$ to 760, $m = 0.905$ or $\delta_{10°}\, m$, 1.74. At 49.2° and $p = 790$, $m = 2.32$ decreasing to 1.17 at $p = 835$ or $\delta_{10°}\, m = 1.84$. At 25.2° and $p = 843$, $m = 0.088$ decreasing to 0.030 at $p = 890$ or $\delta_{10°}\, m = 5.55$. At 35.2° and $p = 892$, $m = 0.073$ decreasing to 0.037 at $p = 894$ or $\delta_{10°}\, m = 2.21$. At 49.5° and $p = 895$, $m = 0.070$ or $\delta_{10°}\, m = 1.35$.

The erratic values of $\delta_{10°}\, m$ indicate that the reaction is very complex in Pyrex as in quartz over a temperature range including that covered by Bodenstein and co-workers.[2,3] The results of these experiments do not lend themselves readily to a kinetic treatment. However, some general conclusions can be made. It is apparent that the more carefully the gases and the reaction system are purified, the more erratic are the results and the more pronounced is the fast reaction. Hamann and Schumacher[3] found some indications of this fast reaction with gases which perhaps were as pure as those used here. This undoubtedly constitutes an agreement between their work and ours. Experiments with sulfuric acid and water point rather against a pure wall reaction as the cause of phenomena here described. It seems instead more likely that an unstable intermediary product (Hamann and Schumacher suggest ClO) accumulates in the absence of impurities and causes a fast decomposition of ozone in a chain reaction which is sensitive to alterations in experimental conditions so minute that they were beyond our control. This last circumstance makes it unprofitable to discuss here the reaction mechanism in greater detail.

The fast reaction observed in our experiments is very probably analogous to the explosions of bromine–ozone mixtures reported by Lewis and Feitkneckt.[9] The difference appears to be in degree only, and attributable to the stability of chlorine oxides, greater than that of bromine oxides, which prevents the production of a real explosion.

Summary

The decomposition of ozone in the presence of chlorine has been reinvestigated at 2. 13 and 22° in quartz and in Pyrex at 23, 35 and 50° with

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[7] Kistiakowsky, *Z. physik. Chem.*, **117**, 337 (1925).

[8] Kassel, Ref. 1f. p. 264.

[9] Lewis and Feitknecht, THIS JOURNAL, **53**, 2910 (1931).

great care in pressure measurement, temperature control and avoidance of contaminations. Each gas was thrice fractionated, stopcocks were eliminated and the cell walls freed from adsorbed impurities. As such precautions became more stringent, the speed of the dark reaction following a brief exposure to light, an increase in temperature or even a period in the dark at 2, 13 or 23° tended to increase surprisingly. After this, an equally striking decrease often occurred.

The time intervening before inception of the fast reaction decreased with an increase in the temperature and was shortened by absorption of light by chlorine. Temperature coefficients became highly abnormal, ranging from 0.7 to 14.6. At the same time the quantum yield, corrected for the dark reaction, fell off from two or more to very small values. Reaction velocities and temperature coefficients sometimes became small again, after which the system tended to regain sensitiveness to light.

Concentrated sulfuric acid or water, within the cell, inhibited but did not eliminate these anomalies. They were at a minimum when greased stopcocks were used in the gas train.

Uncontaminated ozone, without chlorine, gave a fast dark reaction at the start which died down during the first two and one-half hours and could not be restored during the next seven days by light of any available wave length or by temperature changes.

The fact that light is readily capable of starting the "fast" reaction is evidence for the essential similarity, if not identity, of the mechanisms of light and dark reactions.

We have attempted to explain the above observations in terms of a heterogeneous or a homogeneous reaction chain or in terms of a combination of both. No mechanism so far considered by us, including those given in the literature, seems to fit all our experimental data. We, therefore, prefer for the present to reserve their discussion.

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