methyl hydrogens shifts, in the other it is the formate hydrogen.

Summary

The photolysis of methyl formate and methyl acetate has been investigated by means of the mirror method developed by Paneth and others. Free radicals were formed by the esters. No hydrogen atoms were detected. The rates of removal of bismuth mirrors by fragments formed in the decomposition of methyl formate and methyl acetate have been compared with those obtained from acetone. The half-life periods of the free radicals produced by methyl formate and acetone have been computed. The value for the half-life of the fragments from methyl formate was found to be 6–8 $\times 10^{-3}$ and from acetone 2–3 $\times 10^{-3}$ second. The value for acetone showed good agreement with that obtained by other investigators in the pyrolysis of acetone and the value for methyl formate agreed with the value obtained in the thermal decomposition of lead tetramethyl.

The photolysis of methyl formate in a static system has been studied. The products formed in the decomposition were found to be CO, H_2, CH_4, C_2H_6, CH_3OH, and a minute amount of HCHO. The total reaction can be represented as a combination of four net reactions. These are

$$HCOOCH_3 \longrightarrow CH_3OH + CO \quad (1)$$
$$HCOOCH_3 \longrightarrow 2CO + 2H_2 \quad (2)$$
$$HCOOCH_3 \longrightarrow CO_2 + CH_4 \quad (3)$$
$$2HCOOCH_3 \longrightarrow C_2H_6 + H_2 + 2CO_2 \quad (4)$$

The products at 50% decomposition of the ester are such that the total reaction may be considered as made up of approximately 61% of (1), 16% of (2), 15% of (3), and 8% of (4). The effect of nitric oxide has been studied. Mechanisms for some of the net reactions have been suggested.

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

The Thermal and Photochemical Decomposition of Oxalyl Bromide

BY J. E. TUTTLE AND G. K. ROLLEFSON

In most studies of the photolyses of simple organic molecules the effective wave lengths lie so far in the ultraviolet that the absorbed quanta possess sufficient energy to break the molecule into free radicals. Although some of the molecules which have been studied, such as formaldehyde and acetaldehyde, show some variation in behavior as the wave length is varied, it seems reasonable to expect that more marked effects will be found with substances which absorb at longer wave lengths where free radical formation is either impossible or at least improbable. Oxalyl bromide which has an absorption extending from $\lambda > 4358$ to $\lambda < 2537$ Å. seemed a suitable subject for such an investigation. The results of both the photolysis and pyrolysis of oxalyl bromide are presented in this paper.

Materials.—Oxalyl bromide was prepared by bubbling four times the theoretical amount of dry hydrogen bromide through oxalyl chloride at 0°. The oxalyl chloride was obtained from the Eastman Kodak Co. The conversion to the bromide was apparently quite complete since on distillation practically all of the liquid came over at the boiling point of oxalyl bromide, 106°. The middle portion of this distillate was distilled in vacuum over mercury to remove bromine and the middle portion of this distillate was used for our experiments. The purified compound is yellowish-green in color. In "Beilstein" it is reported that a slow decomposition takes place in the dark with the appearance of bromine. This was not found to be true with our material; after three months no appreciable color of bromine had appeared.

Oxygen was prepared by liquefying tank oxygen and distilling off a considerable amount of the liquid. The gas was admitted to the reaction vessel as needed under its own vapor pressure at liquid air temperatures.

Hydrogen was taken from a cylinder, passed over hot copper to remove oxygen and dried with phosphorus pentoxide.

Hydrogen iodide was prepared by dehydrating hydriodic acid with phosphorus pentoxide and distilling over mercury to remove iodine.

Ethylene was taken from a cylinder, dried over phosphorus pentoxide and distilled in vacuum.

Nitrosyl chloride was obtained from Mr. K. Atwood, who had prepared it in this Laboratory by the direct combination of nitric oxide and chlorine.

Hexane was purified by shaking with concentrated sulfuric acid until the acid layer remained colorless. Next it was shaken with acid potassium permanganate and finally with alkaline permanganate. It was dried by distilling over phosphorus pentoxide.

Absorption Spectrum.—Since no absorption spectrum of oxalyl bromide could be found in the literature, measurements were made of the absorption coefficient at various wave lengths.[1] Photographs of the absorption spectrum were taken on a Hilger quartz spectrograph. The absorption cell was of quartz 19.6 cm. long and pressures of 0.6 and 2.4 cm. of mercury of the oxalyl bromide were used. The spectra were photometered on the Zeiss microphotometer belonging to the University of California Physics Department. The photographic plate characteristics were determined by taking photographs of the light source through screens of known transmission. The absorption coefficients were calculated according to the equation $\epsilon = (\log I_0/I)/cl$ in which c is in moles per liter and l in centimeters. The results are plotted in Fig. 1. Determinations were also made for some of the wave lengths present in the mercury arc spectrum; these are shown in Table I.

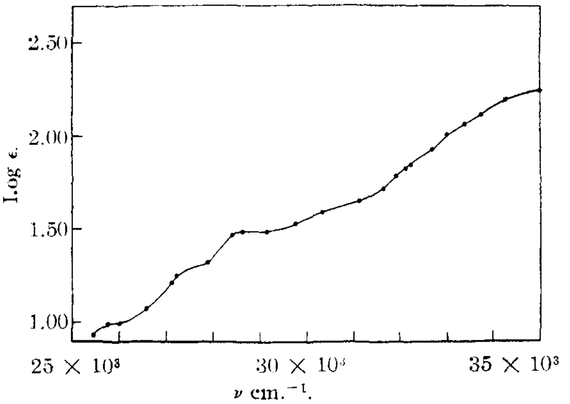

Fig. 1.—Absorption curve for oxalyl bromide.

TABLE I

λ	4358	4047	3660	3130	2652
ε	0.91	2.01	18.3	61.3	227

The absorption curve shows three distinct humps at the long wave length end and a fourth indistinct one can be detected by visual examination of the plates. The separation of the humps is about 1400 cm.$^{-1}$. The same interval is observed in glyoxal, diacetyl[2] and oxalyl chloride[3] and probably corresponds to a fundamental vibration frequency of some part of the molecule probably the carbonyl group. The fundamental frequency of the carbonyl group as determined from Raman spectra is ~1700 cm.$^{-1}$ and this does not seem to be appreciably altered in such a compound as diacetyl.[4] The difference of 1400 cm.$^{-1}$ found by us would be the frequency in a higher electronic state.

Photolysis.—The photolysis of the oxalyl bromide was carried out in a cylindrical quartz reaction cell 5.4 cm. long and 5 cm. in diameter. The volume of the cell is approximately 115 cc. The vessel was connected to the oxalyl bromide reservoir and to the vacuum pumps through glass valves. A glass click gage connected to mercury and sulfuric acid manometers was used in the pressure measurements. The light source was a water-cooled capillary arc of the type designed by Mr. K. Atwood.[5] Various arrangements were used to obtain monochromatic light. At the shorter wave lengths a simple quartz prism monochromator was used. At the longer wave lengths the quartz prism was replaced by a hollow Pyrex prism filled with ethyl cinnamate or, as in some experiments, the arc was used in combination with suitable filters.

Illumination of the oxalyl bromide either with the full light of the arc or with the light of any one of the mercury lines between λ = 4358 Å. and λ = 2652 Å. caused the formation of bromine as was shown by the color of the gas. Furthermore, at all wave lengths except 4047 and 4358 Å. the pressure increased toward a limit three times the initial pressure. At the two wave lengths mentioned as exceptions the absorption by the bromine became so high that the reaction was essentially stopped before the bromide was completely decomposed. These observations are in accord with the equation

$$(COBr)_2 \longrightarrow 2CO + Br_2$$

for the over-all reaction.

In order to determine whether the decomposition proceeds directly to the final products or whether some other substance, such as bromophosgene (*cf.* the thermal decomposition), is present in appreciable concentrations in the intermediate stages, experiments were carried out at the wave lengths 3660, 3130, and 2652 Å. in which the reaction was followed not only by the change in pressure but also by the change in the absorption of λ = 4358 Å. Oxalyl bromide or any product other than bromine which might be formed from it has a very small absorption at the latter wave length, hence the change in the absorption for this wave length is a measure of the bromine formed. Specifically, the logarithm of the ratio of the initial intensity to the intensity at any time is proportional to the bromine pressure. If the oxalyl bromide decomposes directly

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(1) We are indebted to Mr. H. W. Anderson and Dr. M. Calvin for assistance in these experiments.

(2) Light, *Z. physik. Chem.*, **122**, 414 (1926).

(3) Krauskopf and Rollefson, THIS JOURNAL, **58**, 443 (1936).

(4) Hibben, "Raman Effect and its Chemical Applications," Reinhold Publishing Co., New York, N. Y., 1939.

(5) K. Atwood, Ph.D. Thesis, University of California, 1940.

into carbon monoxide and bromine the pressure change is double the pressure of bromine formed. Hence, except for a proportionality factor log I_0/I should equal Δp if the concentrations of any intermediates are negligible. Table II shows how well this proportionality was maintained in an experiment in which the oxalyl bromide was decomposed by λ = 3130 Å. The k tabulated in the fourth column is the proportionality factor just mentioned, *i. e.*, it is the ratio of the numbers in the second column to those in the third. The small value of log I_0/I at zero time corresponds to the absorption by the oxalyl bromide and this effect is responsible for the slight deviations of k from constancy at the start of the reaction. Similar results were obtained with the wave lengths 3660 and 2652 Å. For purposes of comparison at Δp = 10.10 cm. of sulfuric acid the values log I_0/I were 0.294, 0.298, and 0.300 for the wave lengths 3660, 3130, and 2652, respectively. As an additional check on this method of measuring the bromine formed we calculated the absorption coefficient of bromine from our measured log I_0/I and on the assumption that the bromine pressure was equal to $\Delta p/2$. A value of 131 was obtained as compared to 126 given in the "International Critical Tables." This was considered satisfactory agreement since the light beam used in the measurement passed through the cell at an angle, a fact which made it difficult to get an accurate measure of the length of the path through the absorbing gas.

TABLE II

COMPARISON OF AMOUNT OF REACTION AS MEASURED BY PRESSURE CHANGE AND BY LIGHT ABSORPTION

Initial oxalyl bromide pressure, 12.50 cm. H_2SO_4; photoactive wave length, 3130 Å.

Time, minutes	Δp cm. H_2SO_4	log I_0/I (4358)	k
0	0.0	0.007	..
3.1	1.20	.041	29.3
6.0	2.40	.074	32.4
8.6	3.35	.100	33.5
11.6	4.45	.130	34.2
15.6	5.75	.169	34.0
19.0	6.80	.201	33.8
22.5	7.85	.231	34.0
26.2	8.90	.263	33.9
30.7	10.10	.298	33.9
35.0	11.15	.330	33.8

In order to test the hypothesis that the failure of the reaction at wave lengths greater than 4000 Å. to proceed until the pressure was triple the initial pressure, some experiments were carried out with ethylene present. It was shown that in experiments with the full light of the arc the ethylene had no effect on the reaction other than to remove the bromine. In experiments using only the light transmitted by a novial 0 filter it was found that the final pressure increase was equal to the original oxalyl bromide pressure. This fact is in accord with either of the equations

$$(COBr)_2 \longrightarrow COBr_2 + CO$$
$$(COBr)_2 + C_2H_4 \longrightarrow 2CO + C_2H_4Br_2$$

The condensable products were frozen out in a liquid air trap, the trap was transferred to a solid carbon dioxide–acetone-bath and the ethylene pumped off; finally the residue was treated with water and tested for acidity. No acidity was found which indicates that bromophosgene is not formed since that substance hydrolyzes readily in water to form hydrobromic acid and carbon dioxide. It may be concluded, therefore, that the photolysis of oxalyl bromide proceeds to carbon monoxide and bromine at all wave lengths without building up any appreciable concentration of an intermediate.

Quantum Yield.—The quantum yield was determined with the aid of various actinometers. Determinations at the wave lengths, 3650, 3130, and 2652 were carried out by isolating the desired line with the quartz monochromator and measuring its intensity by means of a uranyl oxalate actinometer[6] placed directly in front of the reaction cell. The fraction of the light absorbed by the oxalyl bromide was measured by means of a photocell or calculated from the previously determined absorption coefficients. The amount of reaction was calculated from the pressure change. A second method used at the wave lengths 3130 and 2652 Å. involved the comparison of the rates of photolysis of hydrogen iodide and oxalyl bromide by running them alternately in the same cell. The quantum yield for the hydrogen iodide decomposition was assumed to be 2.[7] Observations at 3650 and 4042 Å. were made by isolating the lines with a monochromator made with a Pyrex prism filled with ethyl cinnamate. A comparison of the rates of photolysis of nitrosyl chloride and the oxalyl bromide was used for these lines. Under these conditions nitrosyl chloride is reported to have a quantum yield of 2.2.[8] Finally, a measurement

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[6] Leighton and Forbes, THIS JOURNAL, **52**, 3139 (1930).

[7] Bodenstein and Lieneweg, *Z. physik. Chem.*, **119**, 123 (1920); Lewis, *J. Phys. Chem.*, **32**, 270 (1928).

[8] Kistiakowsky, THIS JOURNAL, **52**, 102 (1930).

of the quantum yield at 4358 Å. was carried out by using the direct light of the arc through a Zeiss B filter (which isolates this line) and measuring the intensity with a uranyl oxalate actinometer. The results do not agree as well as could be expected but they suffice to show that the quantum yield is approximately one or less at all the wave lengths used. The results are summarized in Table III.

TABLE III

QUANTUM YIELDS FOR THE PHOTOLYSIS OF OXALYL BROMIDE

Actinometer used, Å.	2652	3130	3660	4047	4360
Uranyl oxalate	0.80	1.05	0.75		0.85
HI	0.75	0.56			
NOCl		0.75	0.96	1.0	

Mechanism of the Photolysis.—The magnitude of the quantum yield indicates that we are not dealing with a chain reaction. Furthermore, the retardation caused by the inner filter action of bromine at the longer wave lengths shows that bromine atoms do not bring about the decomposition of oxalyl bromide. There are several possible ways for the photoactivated molecule to break up. The primary step after the absorption of light may yield any one of the following: (1) two COBr radicals, (2) a bromine atom and a COCOBr radical, (3) carbon monoxide and bromine directly, (4) bromophosgene and carbon monoxide. The last possibility is definitely eliminated since we were unable to obtain any evidence for bromophosgene and, particularly at the longer wave lengths, bromophosgene does not absorb strongly enough to decompose as fast as it is formed from the oxalyl bromide until quite an appreciable amount is present. The first two possibilities would yield the final products by breaking up into carbon monoxide and bromine atoms followed by a combination of the atoms to form bromine molecules. It is possible, therefore, to distinguish between the third possibility and the first two by adding a substance which will react with bromine atoms but not with bromine molecules. It was found that under the conditions of our experiments hexane reacts with bromine atoms but not with the molecules; hence some experiments were carried out with hexane present in the reaction mixture. The activating wave length was 3130 Å. since that is not absorbed by bromine and therefore cannot produce bromine atoms from any bromine molecules which might form from the oxalyl bromide. It was found that the alkyl bromides formed condensed out on the cell walls and interfered with quantitative measurements but it was observed that no bromine was formed. Several experiments carried out in liquid hexane with various wave lengths also showed no bromine formation.

The remaining possible primary steps are the split into two COBr radicals or splitting off a bromine atom. The work of Schumacher and Bergmann[9] indicates that COBr is quite unstable. Nothing is known about the properties of such a radical as COCOBr; it is possible that it might break into carbon monoxide and COBr. It was thought that oxygen might react with these radicals in a way similar to the reaction with COCl in photoöxidation of phosgene.[10] Hence some experiments were tried with six times as much oxygen as oxalyl bromide in the reaction mixture at temperatures ranging up to 100°. The oxygen did not affect either the final increase of pressure or the rate of pressure increase. The equality of the rates is shown by a comparison of two experiments run at 50°. In forty minutes the one without oxygen was 26.5% complete and in seventy-five minutes it was 39.5% complete; the corresponding figures for the one with oxygen were 25.5 and 41.0%. The failure to find any effect is additional evidence in favor of a non-chain mechanism. It is probably due to a very rapid decomposition of the radicals into carbon monoxide and bromine atoms.

The Thermal Decomposition.—In order to obtain a comparison of the modes of decomposition of thermally and photochemically excited molecules, a study of the pyrolysis of oxalyl bromide was undertaken. Preliminary experiments showed that the rate is measurable at about 200°. Bromine appears as a product and the pressure increase is double the original bromide pressure as in the photochemical reaction. The ultimate products are carbon monoxide and bromine. A very striking difference was noted between the thermal and photochemical reactions. In the latter it has been shown the bromine formed corresponds exactly to the pressure increase whereas in the thermal reaction it was obvious from even qualitative visual observations that the bromine formed was far short of what would be calculated from the pressure change assuming no intermediates to be formed. A more quantitative study was undertaken.

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(9) Schumacher and Bergmann, *Z. physik. Chem.*, **B13**, 269 (1931).

(10) Rollefson and Montgomery, THIS JOURNAL, **55**, 142 (1933).

The apparatus was exactly the same as that used in the photochemical study except that the reaction vessel was placed inside an electric furnace. The temperature was controlled manually by means of a variable rheostat connected in series with the furnace. Most of the runs were made with a quartz reaction vessel but some were made with a Pyrex vessel in order to test for surface effects. The amount of bromine in the reaction mixture was determined by measuring the absorption of light of wave length 4360 Å. The amount of the oxalyl bromide decomposed by this light during the measurements was negligible.

The only possible intermediate of the stability indicated by the preliminary experiments is bromophosgene. Therefore the changes in the system may be represented by a combination of the two net reactions

$$(COBr)_2 \longrightarrow COBr_2 + CO \qquad (1)$$

$$COBr_2 \longrightarrow CO + Br_2 \qquad (2)$$

The specific reaction rate of (1), k, can be evaluated from measurements of the initial slope of the pressure–time curve. With this value for k, it is possible to calculate, by means of the equation $p = p_0(2 - e^{-k_1t})$, the pressure–time curve which should be obtained if reaction (1) alone occurred. The difference between this curve and the observed pressure–time curve represents the extent to which reaction (2) has progressed. The light absorbed by the bromine is also a measure of the extent to which (2) has progressed so a comparison of the two methods of measurement serves as a check on the assumed steps in the reaction. Table IV illustrates this method of treatment as applied to a run made at 206°. The initial points give a value for k_1 of 0.0247 min.$^{-1}$ for this particular experiment. The second column in the table gives the observed pressure, the third the pressure calculated as indicated, the others are self-explanatory. The ratios in the last column should be the same and it is apparent that they are as constant as could be expected considering the possible errors involved in the calculation. No values for the ratio are listed for the first few points because the difference between p and p_t and the magnitude of the light absorbed are too small to be obtained accurately enough for the ratios to have any significance.

Additional evidence for bromophosgene as the intermediate can be obtained by comparing the rate of decomposition of our intermediate with the measurements of Lenher and Schumacher[11] on the thermal decomposition of bromophosgene. They found the reaction to be a wall reaction hence we cannot expect too close agreement since the calculated constants depend on the nature and dimensions of the reaction vessel. At 215° their value for the specific reaction rate in a quartz vessel was 0.045. This value would be decreased by lowering the temperature to 206°, the temperature of the experiment listed in Table IV. From the data in Table IV we calculate k_2 = 0.0154. We consider this satisfactory agreement.

As a further test for wall effects some experiments were carried out in which the quartz reaction vessel was replaced by a Pyrex cell of about 300-cc. capacity. This change had no effect on the initial rate of increase of pressure. On the other hand, the secondary reaction, the decomposition of bromophosgene, was much slower. This observation is also in agreement with the work of Lenher and Schumacher. We may conclude that the thermal decomposition of oxalyl bromide proceeds through a first order homogeneous decomposition into bromophosgene and carbon monoxide followed by a heterogeneous decomposition of the bromophosgene into carbon monoxide and bromine.

TABLE IV

TYPICAL DATA AND CALCULATIONS FOR A RUN ON THE THERMAL DECOMPOSITION OF OXALYL BROMIDE

Temperature, 206°; quartz reaction vessel

Time, min.	p, press. cm.	p_t 2.46(2 − $e^{-0.0247t}$)	$p - p_t$	log I_0/I	$\frac{p - p_t}{\log I_0/I}$
0.0	2.46	2.46	0.0	0.0	
.7	2.52	2.50	.02	.0	
2.8	2.64	2.62	.02	.007	
5.5	2.78	2.72	.06	.004	
8.1	2.91	2.91	.00	.008	
10.9	3.07	3.04	.03	.010	
14.8	3.24	3.21	.03	.014	
18.8	3.39	3.37	.02	.019	
25.5	3.70	3.61	.09	.028	3.2
36.4	4.07	3.91	.16	.055	2.9
43.3	4.34	4.07	.27	.076	3.5
52.5	4.64	4.24	.40	.114	3.5
66.3	5.10	4.43	.67	.173	3.86
79.1	5.50	4.55	.95	.231	4.11
98.8	5.98	4.70	1.28	.300	4.27
115.5	6.23	4.77	1.46	.342	4.27
143.5	6.57	4.84	1.73	.395	4.38
162.5	6.70	4.87	1.83	.418	4.38
190.3	6.83	4.89	1.94	.440	4.40
232.5	6.99	4.90	2.09	.460	4.55

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[11] Lenher and Schumacher, *Z. physik. Chem.*, **135**, 85 (1928).

Table V gives the values of k_1 at various temperatures. Values from the experiments with a quartz reaction vessel and with the Pyrex one are included. If log k_1 is plotted against the reciprocal of the absolute temperature the slope of the line obtained gives 32,000 calories as the heat of activation for the reaction.

TABLE V

k_1 AS A FUNCTION OF TEMPERATURE

T	472	480.5	487	490	
k_1	0.0112	0.0247	0.0440	0.0568	
T	492	498	509	511	512
k_1	0.0570	0.0940	0.192	0.208	0.172

Some experiments were carried out in which hydrogen was introduced to test for the presence of bromine atoms. It is known that the photoreaction of bromine and hydrogen proceeds readily about 200 through a reaction of the bromine atoms with hydrogen to form hydrogen bromide and hydrogen atoms. In our experiments if hydrogen atoms were formed in this way they would react with the oxalyl bromide and cause an acceleration of the decomposition. No effect was observed in the first stage of the reaction and only a slight acceleration of the decomposition of the bromophosgene. Some other experiments were performed in which oxygen was added in the hope that if any radicals were formed some oxidation to carbon dioxide would be found. No effect was observed.

In the experiments in the Pyrex vessel the decomposition of the bromophosgene was so slow that a condition could be reached in which the cell contained essentially a mixture of carbon monoxide and bromophosgene. Advantage was taken of this fact to test for a photoöxidation of bromophosgene. Oxygen was added and the mixture illuminated with the full light of the mercury arc. The only effect observed was the decomposition of the bromophosgene into carbon monoxide and bromine. Apparently no reaction analogous to the oxidation of phosgene occurs, which is possible if the COBr radical decomposes rapidly.

Discussion.—Although the spatial arrangement of the atoms in oxalyl bromide has not been determined, it is probably similar to that of glyoxal or dimethylglyoxal.[12] That would be a planar or approximately planar arrangement with the bromine atoms *trans* to each other. Such an arrangement would offer little opportunity for the bromine atoms to separate as a bromine molecule. The presence of bromine atoms in the photochemical experiments can be accounted for either by splitting off a bromine atom or by breaking the molecule into two COBr radicals which decompose rapidly. The energy absorbed is always sufficient to break a carbon–bromine bond and may be sufficient to break the carbon–carbon bond. The longest wave length used, 4358 Å., corresponds to only 65.5 kilocalories which is a little lower than the value usually taken for a carbon–carbon bond. Whichever split occurs in the molecule the carbon containing radical breaks down into carbon monoxide and bromine atom so rapidly that no other reaction can be made to occur.

The activation energy of the thermal reaction, 32 kcal., is not sufficient to break any bond in the molecule. The failure to find any evidence for bromine atoms or any radicals is in accordance with this fact. Bromophosgene cannot be formed from carbon monoxide and bromine either photochemically[9] or thermally under our experimental conditions. It follows that when the molecule becomes thermally activated it must undergo a rearrangement which brings both bromine atoms onto one of the carbon atoms and the molecule then splits into bromophosgene and carbon monoxide.

Summary

A study has been made of both the thermal and photochemical decompositions of oxalyl bromide. In both cases the ultimate products are carbon monoxide and bromine. The photochemical reaction was studied at several wave lengths ranging from 4358 to 2652 Å. No variation in the nature of the reaction was observed in this range and the quantum yield was found to be slightly less than unity. Bromine atoms were shown to be present during the course of the reaction. The thermal reaction was shown to be a two-stage process with bromophosgene as an intermediate. The decomposition into bromophosgene and carbon monoxide proceeds at about 200° as a homogeneous first order reaction with an activation energy of 32 kcal. The bromophosgene then dissociates into carbon monoxide and bromine in a heterogeneous reaction.

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(12) LuValle and Schomaker, THIS JOURNAL, **61**, 3520 (1939).