The agreement is a justification of the approximations made. Eyring has justly remarked that one has much more *a priori* reason for making the guesses involved in the application of his method, than in the classical collision theory.

It may be well to illustrate by a sample calculation how the units of the calculated velocity constant are determined by the standard state for the entropy of activation. For example, to calculate the velocity constant in liter per mole-second units at 723°K., one must evaluate the standard entropy of activation at such a pressure that each gas concentration is one mole per liter. The entropy of activation for the standard state of one atmosphere and 723°K. is -35.38 cal./deg.

$$n/V = P/RT = 1$$

or

$$P = 0.08207\ T \text{ atm.}$$

$$\frac{\partial(\Delta S^*)}{\partial P} = -\frac{\partial(\Delta V^*)}{\partial T} = -\Delta n \frac{\partial(RT/P)}{\partial T} = \frac{R}{P}$$

since $\Delta n = -1$. Then $\Delta S^* = -35.38 + R \ln P = -35.38 + 4.575 \lg (0.08207 \times 723) = -27.27$ cal./deg.

$$e^{-27.27/R} = 1.095 \times 10^{-6}$$

Then by Equation 1 K is equal to 5.21×10^{-3} liter-mole^{-1}-sec.$^{-1}$.

Naturally the operation involved above is equivalent to the ordinary conversion; thus to obtain the constant at 723°K. in liter-mole^{-1}-second^{-1} units from the calculated constant in atm.$^{-1}$-sec.$^{-1}$ units, one divides the latter by the number of moles/liter per atmosphere.

$$K_{723}(\text{liter-mole}^{-1}\text{-sec.}^{-1}) = K_{723}(\text{atm.}^{-1}\text{-hr.}^{-1}) \times$$
$$\frac{RT}{3600} \text{ (atm./mole/l.)}$$

$$= \frac{0.316 \times 0.08207 \times 723}{3600} = 5.21 \times 10^{-3} \text{ liter-mole}^{-1}\text{-sec.}^{-1}$$

Summary

1. The rate of the homogeneous thermal polymerization of ethylene has been calculated in satisfactory accord with experiment by means of Eyring's activated complex method, using simple assumptions concerning the entropy of activation.

2. The dependence of the units of the rate constant upon the standard state for the entropy of activation is emphasized.

The Photolysis of Acetyl Bromide

BY D. H. ETZLER AND G. K. ROLLEFSON

The photolysis of acetaldehyde has been studied extensively.[1] Although there is agreement as to the experimental data there has been much controversy over the interpretation of the facts. One theory considers that the step following the absorption of the light is a direct rearrangement into the ultimate products carbon monoxide and methane. Another theory assumes that the photo-activated molecule breaks into free radicals and the final products are formed as a result of secondary reactions involving these radicals. Some of the objections to any interpretation which limits itself to a single type of primary process have been discussed in a previous paper.[2] In order to secure additional experimental data which would aid in the determination of the nature of the primary processes, it seemed

desirable to study the photolyses of analogous compounds. Acetone, in which the hydrogen in the aldehyde group of acetaldehyde has been replaced by a methyl radical, has been studied repeatedly.[3] It appears to yield free radicals somewhat more readily than acetaldehyde but the data suggest that decomposition also occurs by way of a rearrangement mechanism, particularly at the longer wave lengths in the absorption band. In this paper we are presenting data on the photolysis of acetyl bromide which differs from acetaldehyde in that the aldehyde hydrogen has been replaced by a bromine atom.

The literature contains no data on the photochemistry of the acetyl halides but some work has been done on the absorption spectra of the chloride and bromide.[4] The latter is reported to have

(1) (a) Leighton and Blacet, THIS JOURNAL, **55**, 1766 (1933); (b) Leermakers, *ibid.*, **56**, 1537 (1934); (c) Pearson and Purcell, *J. Chem. Soc.*, 1151 (1935); (d) Blacet and Roof, THIS JOURNAL, **58**, 278 (1936); (e) Blacet and Volman, *ibid.*, **60**, 1234 (1938).

(2) Rollefson, *J. Phys. Chem.*, **41**, 259 (1937).

(3) (a) Damon and Daniels, THIS JOURNAL, **55**, 2363 (1933); (b) Norrish, Crone and Saltmarsh, *J. Chem. Soc.*, 1456 (1934); (c) Leermakers, THIS JOURNAL, **56**, 1900 (1934); (d) Spence and Wild, *J. Chem. Soc.*, 352 (1937); (e) Matheson and Noyes, THIS JOURNAL, **60**, 1857 (1938).

(4) Rao and Samuel, *Current Sci.*, **3**, 549 (1935).

a continuous absorption with a maximum at 2500 Å. Our own observations made with a 20 cm. long quartz tube and acetyl bromide pressures ranging fom 1 to 70 mm. of mercury show no signs of structure in the spectrum. Extrapolation of the measured absorption coefficients[5] indicates that the absorption begins at approximately 3100 Å. and rises toward shorter wave lengths with some evidence of the maximum reported at ~2500 Å. No visible fluorescence is excited by the light absorption.

Experimental

Kahlbaum acetyl bromide was purified by two fractional distillations. The fraction boiling at 75.7 to 75.8° was shaken with a small amount of mercury and then distilled under vacuum, by means of liquid air, in order to remove traces of a light yellow impurity, very likely bromine, which always appeared upon any considerable exposure of the acetyl bromide to the air. The colorless center fraction resulting from the vacuum distillation was retained and stored as liquid in a bulb which was connected to the reaction vessel and vacuum line through greaseless glass valves. Gas density measurements gave an average molecular weight of 122.5 ± 1.5 (theoretical 122.94) for the vapor at room temperature. It is therefore evident that the vapor consists of single molecules.

To ensure working with acetyl bromide pressures below that of saturation at the temperatures of the various runs, rough vapor pressure measurements were made. At 25° a value of approximately 11 cm. of mercury was found.

In studying the general nature of the photolysis, the reaction vessel used was quartz, cylindrical in shape, 9.70 cm. long and 2.72 cm. in diameter. The volume of the vessel and adjoining tubing was 66.0 cc. The reaction chamber was connected by a glass capillary to the acetyl bromide reservoir and to the vacuum pumps, through the glass valves mentioned above. These valves were similar to the type described by Bodenstein[6] but with silver chloride as a seating material.

Pressures in the reaction vessel were measured by means of a glass click gage[7] connected externally to a mercury manometer and a sulfuric acid manometer. The use of the click gage and glass valves eliminated any contamination of the acetyl bromide which might be caused as a result of contact with stopcock grease or a manometer liquid. The temperature of the gas in the reaction vessel was maintained constant during experiments to within 1 or 2° by running tap water over the vessel. The temperatures, controlled in this manner, ranged from about 14 to 22° in different experiments. This variation had no apparent effect on the nature or rate of the reaction. The heating effect of the light source was negligible when a rapid stream of cooling water was run over the reaction vessel.

The light source employed in studying the general course of the photolysis was a spiral quartz mercury arc, designed

to give relatively high intensity of the 2537 Å. line of the mercury spectrum. The arc was made for this research by the Electro Therapy Products Corporation of Los Angeles and was checked in this laboratory for intensity of the 2537 Å. line by taking spectrograms. The arc was of such dimensions that it fitted easily over the entire length of the reaction vessel and it was used in that manner during the majority of experiments carried out with it.

A typical run was made in the following manner. The cooling water was run over the reaction vessel until its temperature became steady and then the desired pressure of acetyl bromide was introduced. Because the arc required at least a minute to reach full intensity, a piece of brass pipe was fitted over the reaction vessel, inside the arc, and was held there for a minute or more after the source had been turned on. A stop watch was started at the instant the brass pipe was removed and pressure readings were taken at various time intervals. The reaction products of the photolysis were partly condensed at liquid air temperatures. Among the substances thus condensed was always a light yellow solid, which upon warming of the reaction vessel liquefied and vaporized. The liquid air "freeze-outs," for which a temperature correction factor was determined, indicated a pressure of noncondensable gas approximately 1.15 times that of the initial acetyl bromide pressure. Within experimental error, the limiting pressure in the decomposition was always double the initial pressure in all cases where the reaction was followed to completion.
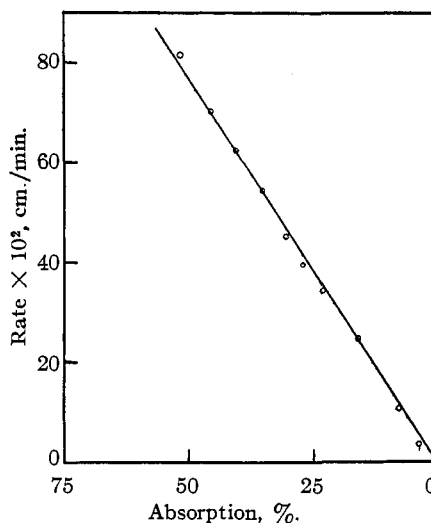

Fig. 1.

In Fig. 1 the rate, determined by measuring slopes of a total pressure–time curve, has been plotted against the light absorbed for a run in which the initial pressure of acetyl bromide was 3.99 cm. of mercury. The percentage of light absorbed was calculated by assuming that none of the acetyl bromide in the click gage or connecting leads reacted during the time of these measurements and that the change of pressure measured the amount of acetyl bromide decomposed in the reaction vessel. The average light path was taken as 2.72 cm. and the absorption coefficient of the acetyl bromide for λ = 2537 Å. was taken as

(5) Etzler and Rollefson, J. Chem. Phys., 6, 653 (1938).

(6) Bodenstein, Z. physik. Chem., 7, 387 (1930).

(7) Smith and Taylor, This Journal, 46, 1393 (1924).

Table I

Density of Gases Condensed by Liquid Air

Temp., °C.	15.2	16.2	15.0	14.7	
(A) $P_{initial}$, AcBr, cm. H_2SO_4	43.87	39.54	42.66	41.37	
(D) P_{final}	87.67	78.94	85.32	82.98	
(C) P_{final} at liq. air temp. $\times$ 3.50	51.30	43.30	50.00	46.50	
(B) P after pumping at liq. air temp.	40.84	37.39	37.96	38.95	
Wt. of sample, g.	0.0499	0.0448	0.0479	0.0482	
Av. mol. wt., g.	101.2 ± 1.5	101.7	101.7	101.7 ± 1.0	Av. = 101.6 ± 1.5
A/B	1.073	1.056	1.123	1.062	Av. = 1.079
A/(D − C)	1.205	1.108	1.207	1.33	Av. = 1.163
% Br_2	...	0.29	0.51	0.36	

64.8.[5] It is evident that the rate is directly proportional to the light absorption over a very wide range.

The products of the photolysis which were not condensable with liquid air were analyzed by means of the microtechnique developed by Blacet, Leighton and others.[8] The procedure was to immerse the reaction vessel in liquid air at the conclusion of an experiment and then open the vessel to a Toepler pump by means of which the gases could be transferred into the analytical apparatus. Samples were analyzed from experiments in which the degree of completion of the reaction ranged from 0.2 to complete. The non-condensable gas was found to be 90 ± 2% carbon monoxide with the balance methane. Tests for hydrogen, ethane and ethylene yielded negative results. Furthermore, the composition of the gas did not vary with the degree of completion of the reaction. The total pressure of non-condensable gas was determined by immersing the reaction vessel in liquid air and correcting the observed pressure to room temperature by an empirically determined "freeze-out" factor. The pressure of non-condensable gas was found to be proportional to the pressure change caused by the reaction at all degrees of completion. This fact shows that the nature of the photolysis does not change in the course of an experiment.

The products of the photolysis which were condensable by liquid air were studied by means of gas density measurements. In order to collect large samples of the gas a quartz bulb of about 412 cc. capacity was used as a reaction vessel, and two spiral mercury arcs were employed as light sources. The reaction in each case was run to completion, requiring approximately five hours under the conditions of the experiments. In obtaining a sample of the desired gases the bulb was immersed in liquid air and opened to the vacuum pumps for a period of from twenty-five to thirty minutes, in one case with several interruptions during which the vessel was warmed and then re-immersed in liquid air. Pumping longer than the stated period did not affect the results of the measurements, but shorter periods gave low values for the average molecular weight, ranging from 87 to 96, depending on the time of pumping. The results of four density measurements are summarized in Table I. The pressures were all read at the same temperature in a given run (except for the liquid air freeze-outs).

All of the bromine, in whatever form it may be in the

products of the photolysis, can be safely assumed to be retained in the fraction condensed by liquid air. Hence the ratio A/B of Table I is indicative of the fact that these gases must contain approximately 8% of molecules in which there are two bromine atoms, or a smaller per cent. of molecules with higher bromine content. Another measure of the pressure of the condensable gases is obtained from D − C. The errors involved in the two determinations have opposite effects. The pressure B may be too high on account of incomplete removal of dissolved non-condensable gases. On the other hand, any incompleteness in freezing out the condensable material would make C too high and in this case the error in measurement is multiplied by 3.5. Hence A/B may be considered a minimum value and A/(D − C) a maximum for the ratio of the initial acetyl bromide pressure to the final pressure of condensable substances. The main constituent of the condensable material is evidently methyl bromide (mol. wt. 94.94). Free bromine was proved present by shaking the gases with water, after density measurements had been made, and testing the resulting solution with potassium iodide and starch. The liberated iodine was titrated with 0.01 N thiosulfate solution, but the percentages of bromine thus estimated (see Table I) can only be taken as minimum values. They are undoubtedly low because of the difficulty of handling the samples in such a way as to avoid losses. The bromine accounts for the yellow color of the solid observed in liquid air freeze-outs.

Qualitative tests on water solutions of the gases condensable in liquid air were negative for hydrogen ion (from AcBr or HBr) carbonate ion (from CO_2) and oxalate ion (from $(COBr)_2$, which, however, is probably unstable at the wave lengths used here). Bromide ion tests were always very positive.

The rate of the photolysis of acetyl bromide at temperatures of 50–55°, attained by allowing the reaction vessel to be heated by the spiral arc, was essentially the same as that at the lower temperatures.

The Effect of Nitric Oxide.—Nitric oxide was prepared by a simple modification of the method used by Johnston and Giauque[9] in obtaining the pure compound for their heat capacity measurements. Two molal sodium nitrite was dropped into a three molal potassium iodide solution which was acidified with sulfuric acid. The generator was evacuated before any sodium nitrite was introduced. The nitric oxide was generated as needed, bubbled through concentrated (18 M) sulfuric acid and passed through a

(8) Blacet and Leighton, Ind. Eng. Chem., Anal. Ed., 3, 766 (1931); Blacet, MacDonald and Leighton, ibid., 5, 272 (1933); Blacet and MacDonald, ibid., 6, 334 (1934); Blacet and Volman, ibid., 9, 44 (1937).

(9) Johnston and Giauque, This Journal, 51, 3194 (1929).

phosphorus pentoxide tube before it entered the reaction vessel. No nitrogen dioxide was ever observed in the generating system. For a number of the initial experiments the nitric oxide was prepared by the method of Biltz and Biltz.[10] The general procedure in these experiments was the same as that employed with pure acetyl bromide. The reaction vessel was filled to the desired pressure with acetyl bromide and then the nitric oxide was introduced, about five minutes being the usual time allowed for mixing. A series of runs was made in which the initial acetyl bromide pressure was the same to within ~15% and the nitric oxide pressure was varied from 6% to about 300% of the initial acetyl bromide pressure. The results obtained are represented by Fig. 2, which shows the effect of nitric oxide on the change of pressure observed in a reaction.

Though at the lowest pressures of nitric oxide no visible changes occurred in the reaction mixture, at the higher pressures a brown gas (probably bromine or nitrosyl bromide) seemed to be formed and a light yellow condensate appeared on the walls of the reaction vessel, both within a minute. The initial rate of pressure decrease in these runs was essentially the same as that of pressure increase in the normal photolysis. The period of illumination was from five to fourteen hours in different runs. At the high nitric oxide pressures, following attainment of the limiting pressure decrease, liquid air freeze-outs indicated a pressure of non-condensable gas corresponding to ~60 to 70% of the initial acetyl bromide pressure. In the first minute or two of the reaction a fine white mist was noticeable in the reaction vessel if the arc was turned off.

The gaseous products of the reaction which were not condensable in liquid air were analyzed by the microanalytical procedure described for the photolysis of pure acetyl bromide. Excess nitric oxide was converted into nitrogen dioxide by adding excess oxygen, and then the dioxide was removed with a bead of solid potassium hydroxide. At low nitric oxide pressures the analyses showed that the composition of the non-condensable products was identical with that obtained with pure acetyl bromide. At higher pressures of nitric oxide no hydrocarbon was formed.

Quantum Yields.—In order to determine the quantum yield at $\lambda = 2652$ Å. the light of an Hereaus type quartz mercury arc was spread into a spectrum by means of a simple fused quartz monochromator designed and constructed in this Laboratory. The purity of the radiation passing through the reaction vessel was tested by taking spectrograms of the beam. The slits of the monochromator were adjusted until this test showed only small amounts of radiation other than that desired. Since the light intensity obtained in this was much less than that used in the experiments at $\lambda = 2537$ Å. with the spiral arc, the cylindrical reaction vessel was replaced by a small rectangular vessel. The path of the beam through

(10) H. Biltz and W. Biltz, "Laboratory Methods of Inorganic Chemistry," translated by Hall and Blanchard, John Wiley and Sons, Inc., New York, N. Y., 1909, p. 204.
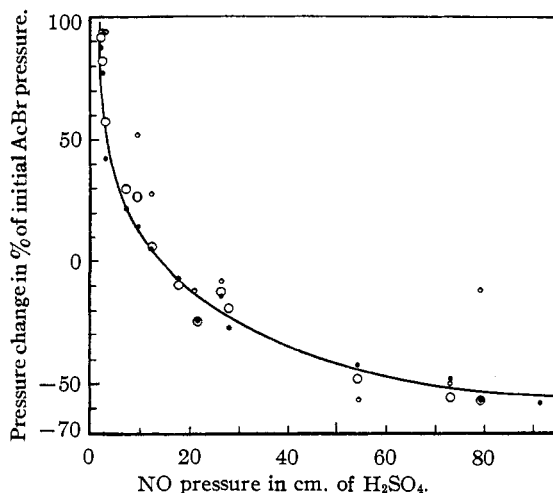

Fig. 2.—The effect of nitric oxide on the photolysis of acetyl bromide: ●, change after one hour of exposure; ◐, change after two hours of exposure; ○, change at completion of experiment.

this vessel was 2.40 cm. in length and the volume of the vessel and connecting tubing was measured and found to be 34.77 cc. The average rate of energy input was determined by means of a uranyl oxalate actinometer cell,[11] which was placed immediately behind the reaction chamber and exposed to the radiation for a measured interval. Using 0.582 for the quantum yield of the oxalate decomposition and allowing 10% for absorption and reflection losses caused by the rear window of the reaction cell, an average figure of 4.03×10^{14} ($\pm 0.12 \times 10^{14}$) quanta per second was found for the energy entering the reaction vessel. Verification of this value was obtained by means of another known reaction, the oxidation of phosgene,[12] which was carried out in the reaction vessel itself. Using a value of 1.8 for the quantum yield of this reaction and 5.94 for the absorption coefficient at 2652 Å., the rate of energy input was calculated to be approximately 5×10^{14} quanta per second. The small pressure changes in the phosgene oxidation made the results less reliable than those obtained using uranyl oxalate, but they constitute an approximate check.

The number of acetyl bromide molecules reacting was calculated from the pressure change on the assumption that $P_{acetyl\ bromide} = P_{final} - P_t$. ($P_{acetyl\ bromide\ decomposed} = P_t - P_{initial} = \Delta P$.) This relationship is justified on the basis of the pressure doubling which occurs in the de-

(11) Leighton and Forbes, THIS JOURNAL, 52, 3139 (1930).
(12) Rollefson and Montgomery, ibid., 55, 142 (1933).

composition (see Fig. 1) and receives further support in the fact that no difference in the composition of the products was observed at various stages of the reaction. Using the value $\epsilon = 46.8$ for the absorption coefficient at 2652 Å., and the uranyl oxalate figure for the rate of energy input, the quantum yields calculated for seven experiments were 0.55 ± 0.13.

Microanalyses were carried out on the non-condensable gases produced in several of the runs at 2652 Å. and for two experiments in which the incident radiation included the wave lengths 2750 to 3700 Å. The absolute accuracy of the analytical results was hampered by the small volumes of gas which were left for combustion after carbon monoxide had been absorbed out by silver oxide. There was always a residue of non-combustible gas, which was probably air introduced during handling of the samples. The presence of the inert gas also was indicated by the fact that the total volume of non-condensable gas as actually measured was somewhat high compared to the volume expected on the basis of the pressure change. Though the data cannot be said to be precise on account of these difficulties, a comparison of the carbon monoxide percentages to those obtained in a similar manner at 2537 Å. with the spiral arc indicates a trend toward higher values at the longer wave lengths. ($93 \pm 2\%$ CO for $\lambda = 2652$ Å. and approximately the same for $\lambda > 2750$ Å.)

The quantum yield of the decomposition of acetyl bromide at 2537 Å. was determined by means of experiments employing the spiral arc. The very high relative intensity of the 2537 Å. radiation from this arc permitted using it as essentially a source of monochromatic light of this wave length. The data for calculating the quantum yield were obtained (1) by comparison of the initial rate of the acetyl bromide decomposition with that of the oxidation of phosgene conducted under identical conditions and (2) by measuring the intensity of the spiral arc with the uranyl oxalate reaction. The first method can be illustrated by the following sample calculation: with initial pressures of 4.64 and 6.41 cm. for acetyl bromide and phosgene, respectively, the rates at fifteen seconds as read from the rate curves were 0.96 and 1.32 cm. per minute. The absorption of light at fifteen seconds was 64.4% for acetyl bromide and 25.3% for phosgene. Taking Montgomery and Rollefson's value[12] for the

quantum yield of the phosgene oxidation, 1.8, and assuming that for the decomposition of acetyl bromide to be 1, the rate of the latter reaction should be $64.4/25.3 \times 1/1.8$ or 1.41 times that of the former. Actually the ratio of the rates was 0.73, so that the quantum yield is not 1 but $0.73/1.41$ or 0.52 for the decomposition of acetyl bromide. Ten such comparisons of rates yielded values for γ of 0.55 ± 0.2. The retarding effect of chlorine in the oxidation of phosgene was minimized by using an excess of oxygen.
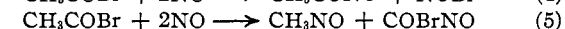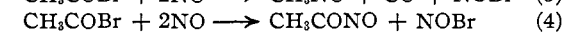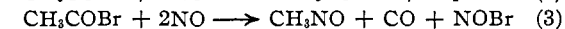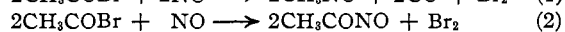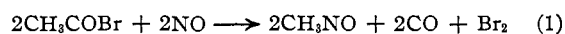
The second method of determining the quantum yield of the acetyl bromide decomposition at 2537 Å. constituted an independent check on the first method. The same cylindrical reaction vessel used in the experiments with acetyl bromide (and the phosgene oxidation) was cut from the vacuum line and filled with uranyl oxalate. The cell was exposed to the spiral arc in the same manner employed with acetyl bromide. Using five-minute exposures, the average titration of the oxalate solution was 51.30 ± 0.2 cc. of 0.09975 N potassium permanganate as compared with 60.47 ± 0.02 cc. for the unexposed solution. Using this datum and 0.602 for the quantum yield of the oxalate decomposition (the value given for 2550 Å. by Leighton and Forbes[11]), the average number of quanta striking the cell–solution interface per second was found to be 1.54×10^{18}. The number of acetyl bromide molecules reacting was calculated from the pressure change and the volume of the system (66.0 cc.). The average absorption was calculated from the absorption coefficient, assuming an average light path of 2.72 cm. The average value of γ, 0.46, is in fair agreement with that of 0.53 found by the first method. The value of 0.53 found at 2652 Å. indicates that no significant change occurs in going from 2537 to 2652 Å. Refined measurements will be necessary to detect a definite trend if it exists.

Discussion

Since the rate of the photochemical decomposition of acetyl bromide depends only on the light absorbed (cf. Fig. 2), conclusions concerning the mechanism of the reaction must rest primarily on other observations. The experiments in which nitric oxide was added to the system are of particular importance with reference to the nature of the primary step in the decomposition. The interpretation of the results is based on the

assumption that nitric oxide reacts only with free radicals in the system studied. This assumption has been used by others[18] both in thermal and in photochemical investigations.

The photodecomposition of pure acetyl bromide results in a 100% increase of pressure. Figure 2 shows that when nitric oxide is present the pressure increase is less and finally becomes a pressure decrease which in the limit is somewhat more than 50% (~60%) of the initial acetyl bromide pressure. The pressure decrease is attributed to the precipitation of a compound of the type RNO, formed from a free radical and a nitric oxide molecule. The available information concerning such products is extremely limited. There is evidence in the work of Thompson and Linnett[13c] (cf. also 13d) on the photolysis of a mixture of mercury dimethyl and nitric oxide, for the formation and condensation of CH_3NO, which apparently is stable at 25° and to light of 2537 Å. wave length. CH_3NO is isomeric with formaldoxime and with formamide and could be expected to isomerize readily to the former.[14a] Formaldoxime forms a termolecular polymer,[14b] hence it is possible to remove methyl radicals in the form of a solid by this method. In the photolysis of acetyl bromide nitric oxide may react with methyl radicals in this manner or it may react with acetyl radicals or bromine atoms. The nitrosyl bromide formed in the latter instance is volatile at the temperatures prevailing in our experiments. Nothing is known about any compound which might be formed from acetyl radicals and nitric oxide. Asssuming that the free radicals formed react with nitric oxide, the following net reactions must be considered

$$2CH_3COBr + 2NO \longrightarrow 2CH_3NO + 2CO + Br_2 \quad (1)$$
$$2CH_3COBr + NO \longrightarrow 2CH_3CONO + Br_2 \quad (2)$$
$$CH_3COBr + 2NO \longrightarrow CH_3NO + CO + NOBr \quad (3)$$
$$CH_3COBr + 2NO \longrightarrow CH_3CONO + NOBr \quad (4)$$
$$CH_3COBr + 2NO \longrightarrow CH_3NO + COBrNO \quad (5)$$

If the products CH_3NO and CH_3ONO are considered as non-volatile, and it is assumed that all of the acetyl bromide is decomposed into free radicals, the final pressure decreases to be expected on the assumption that only one of these reactions is involved are 50, 150, 100, 200 and

200% of the initial acetyl bromide pressure for the reactions in the order listed.

The pressure change alone is not sufficient to determine the relative importance of the five reactions. Reaction (5) may be considered unimportant since there is evidence that COBr is very unstable.[15] Further evidence concerning the other reactions is obtained from the determination of the non-condensable gas present after the limiting pressure decrease was attained in the experiments with excess nitric oxide. This gas was mainly carbon monoxide. Some nitric oxide is also present as this gas is not completely frozen out at liquid air temperatures. If it is assumed that the partial pressure of nitric oxide in these freeze-out experiments is the same as that of pure nitric oxide, i. e., about 3 mm., then the final pressure of carbon monoxide may be as low as 40 or 50% of the initial pressure of acetyl bromide. The failure to obtain one mole of carbon monoxide for each mole of the acetyl bromide decomposed indicates that the reactions (1) and (or) (3) cannot account for all of the decomposition. Reaction (2) or (4) or both must be involved. However, it is not sufficient to consider only the latter two reactions, as they must be accompanied by some process which produces carbon monoxide. Such a process could be one or more of the following: (a) a reaction of the type (1) or (3); (b) a rearrangement; (c) a decomposition of CH_3CONO. The last of these possibilities cannot be of much importance since our results show that such a decomposition is not complete and this lack of completeness is not due to the slowness of decomposition. If an incomplete reaction of this type results from the attainment of equilibrium, the final carbon monoxide pressure should be a constant and not dependent on the initial acetyl bromide pressure.

The absence of methane from the non-condensable gaseous products in the runs with relatively high nitric oxide pressures is evidence that the hydrocarbon is formed in a secondary reaction of free radicals. If it is assumed that the methane is formed by a reaction of methyl radicals with acetyl bromide molecules, it follows that the amount of methane produced may be taken as a measure of the number of molecules of acetyl bromide breaking to form methyl radicals. Although this is an assumption, it is a reasonable one

(13) (a) Staveley and Hinshelwood, Proc. Roy. Soc. (London), A154, 335 (1936); (b) Linnett and Thompson, Trans. Faraday Soc., 33, 501 (1937); (c) Thompson and Linnett, ibid., 33, 874 (1937); (d) Davis, Jahn and Burton, THIS JOURNAL, 60, 10 (1938).

(14) Sidgwick, Taylor and Baker, "The Organic Chemistry of Nitrogen Compounds," Oxford University Press, Oxford, 1937: (a) pp. 169, 204; (b) p. 172; (c) p. 198.

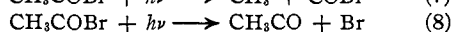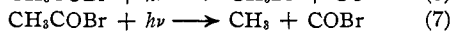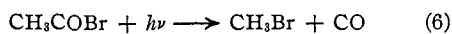(15) Schumacher and Bergmann, Z. physik. Chem., B13, 269 (1931).

and leads to the conclusion that 11% of the molecules absorbing light must react according to either (1) or (3). With the aid of this idea and the maximum pressure decrease in the presence of nitric oxide, it becomes possible to calculate distributions of the reacting molecules among the reactions (1) to (4) and through non-free radical mechanisms. The results are shown in Table II; each column represents a possible distribution. The figures in column IV are probably the nearest to the actual situation as it is more reasonable to suppose that nitrosyl bromide is an ultimate product than to assume the co-existence of nitric oxide and bromine.
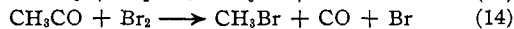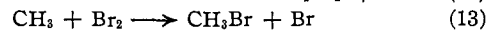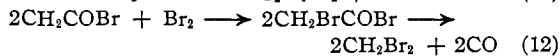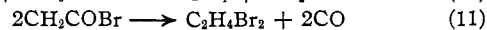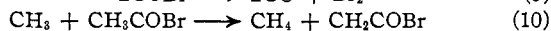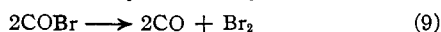
TABLE II

PERCENTAGES OF THE PHOTOACTIVATED MOLECULES WHICH DECOMPOSE ACCORDING TO REACTIONS (1) TO (4) AND NON-FREE RADICAL MECHANISMS

Reaction	I	II	III	IV
(1)	11	11	..	..
(2)	57	..	55	..
(3)	..	..	11	11
(4)	..	48	..	46
Non-free radical	32	41	34	43
Total free radical	68	59	66	57

In the absence of nitric oxide any reaction mechanism which is written must account for the observed products and the pressure doubling and also allow a reasonable explanation for a quantum yield appreciably less than unity. On the basis of our previous discussion three primary steps must be considered
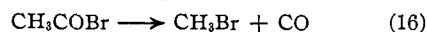
$$CH_3COBr + h\nu \longrightarrow CH_3Br + CO \quad (6)$$
$$CH_3COBr + h\nu \longrightarrow CH_3 + COBr \quad (7)$$
$$CH_3COBr + h\nu \longrightarrow CH_3CO + Br \quad (8)$$

These are followed by secondary reactions such as

$$2COBr \longrightarrow 2CO + Br_2 \quad (9)$$
$$CH_3 + CH_3COBr \longrightarrow CH_4 + CH_2COBr \quad (10)$$
$$2CH_2COBr \longrightarrow C_2H_4Br_2 + 2CO \quad (11)$$
$$2CH_2COBr + Br_2 \longrightarrow 2CH_2BrCOBr \longrightarrow$$
$$2CH_2Br_2 + 2CO \quad (12)$$
$$CH_3 + Br_2 \longrightarrow CH_3Br + Br \quad (13)$$
$$CH_3CO + Br_2 \longrightarrow CH_3Br + CO + Br \quad (14)$$
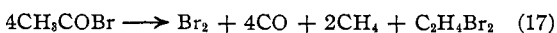$$Br + Br \longrightarrow Br_2 \quad (15)$$

It is not possible to distinguish between methyl bromide and carbon monoxide formed by the direct decomposition (6) and that formed by the sequence (8), (14), (15) or by (7), (9), (13),

(15). The result of the series of reactions may be represented by writing the net reactions

$$CH_3COBr \longrightarrow CH_3Br + CO \quad (16)$$

combined with

$$4CH_3COBr \longrightarrow Br_2 + 4CO + 2CH_4 + C_2H_4Br_2 \quad (17)$$

or

$$4CH_3COBr \longrightarrow 4CO + 2CH_2Br_2 + 2CH_4 \quad (18)$$

Either combination is in accord with the observed doubling of the initial pressure. In order to account for the observed amount of bromine in the products it must be assumed that both of the net reactions (17) and (18) occur. In terms of the mechanism given this means that both (11) and (12) occur to an appreciable extent. A calculation of the molecular weight of the condensable gases gives approximately 104 as compared to 101.6 ± 1.5 observed. The deviation is in the direction to be expected on account of the difficulty of removing the more volatile substances completely.

The absence of any evidence for the formation of diacetyl or ethane indicates that the radicals CH_3 and CH_3CO are removed by reactions such as (13) and (14).

Summary

The photolysis of acetyl bromide at 2537 and 2652 Å. has been investigated. The reaction is directly proportional to light absorbed and the indicated products are CO, CH_3Br, CH_4, Br_2 and $C_2H_4Br_2$. The effect of nitric oxide on the photolysis has been studied. Quantum yields at the two above wave lengths were measured and found to have average values of about 0.5. The results have been discussed in terms of a mechanism which assumes three parallel primary steps. Two of these result in the formation of free radicals and the third involves the direct decomposition of the activated molecule into the final products. The relative proportions of the assumed initial steps have been indicated.