results indicate that the reduction is due to a primary production of an activated form of hydrogen peroxide from the water. Traces of organic substances increase the action of the rays catalytically.

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The Photolysis of Gaseous Acetone and the Influence of Water[1]

BY GLENN H. DAMON AND FARRINGTON DANIELS

The action of ultraviolet light on the simplest ketone offers interesting material in the study of kinetics and photochemistry. Quantitative measurements recorded here show that only about one quantum out of every five or six absorbed produces chemical change in gaseous acetone and that this ratio is affected by pressure, intensity of radiation and other factors. Activated acetone molecules may undergo chemical decomposition, but if water is present as a catalyst they are more apt to undergo a condensation reaction.

Henri and Wurmser[2] and Porter and Iddings[3] found that acetone absorbs between 3400 and 2200 Å. with a maximum at about 2800 Å. Porter and Iddings found also that the rate of decomposition into ethane and carbon monoxide was independent of wave length in this region.

Bowen and Watts[4] using light that was not monochromatic reported a quantum yield of 1.8 molecules per quantum. In the present investigation with better apparatus a much smaller yield was obtained.

Apparatus

Monochromatic light at intensities up to 100,000 ergs per second was obtained with a large quartz monochromator[5] and quartz capillary lamps[6] of high intensity. The monochromator was adjusted to give a sharp focus of a line (3130 Å. for example) on a piece of fluorescent uranium glass placed directly behind the slit. The entrance and exit slits were set at 0.6 mm., a width slightly less than the image of the arc. Back of the slit at a distance of 5 cm. a double convex lens of quartz rendered the monochromatic beam parallel. The beam then passed through a quartz window, into a water thermostat controlled to 0.01°. Here it passed through a narrow, rectangular quartz cell and onto a large thermopile connected to a sensitive galvanometer.

The all-quartz reaction cell, made by the Hanovia Chemical Manufacturing Company, is shown in Fig. 1. It consisted of a rectangular box 10 × 1 × 5 cm. with the

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[1] More complete details of this investigation are contained in part of a Ph.D. thesis by Glenn Damon filed in the Library of the University of Wisconsin in June, 1932.

[2] Henri and Wurmser, *Compt. rend.*, **156**, 1013 (1913).

[3] Porter and Iddings, THIS JOURNAL, **48**, 40 (1926).

[4] Bowen and Watts, *J. Chem. Soc.*, 1607 (1926).

[5] Heidt and Daniels, THIS JOURNAL, **54**, 2384 (1932).

[6] *Ibid.*, p. 2381.

two ends especially clear and optically plane to within 2 mm. of the sides. A dummy cell, identical in dimensions, containing air, was mounted beside the reaction cell and shifted back and forth into the beam of light in front of the thermopile. Actual experiments showed that both cells transmitted 92% of the total incident light if the outer faces were in contact with water. This value agrees closely with the transmission calculated from Fresnel's law.

The pressure diaphragm[7] A was made entirely of quartz with contacts of platinum wire fused and anchored in thin capillaries. It withstood complete evacuation of the cell and was reproducible to 0.2 mm. The air pressure on the outer side of the diaphragm was read on a closed-end mercury manometer with the help of a cathetometer and vernier. A drying tube of calcium chloride in the manometer line prevented the condensation of water on the contacts when the cell was immersed in ice water. A series of capillaries and stopcocks made it possible to change the air pressure very slowly when near a balance. The pressure was read just as the contact was made and the galvanometer needle deflected.

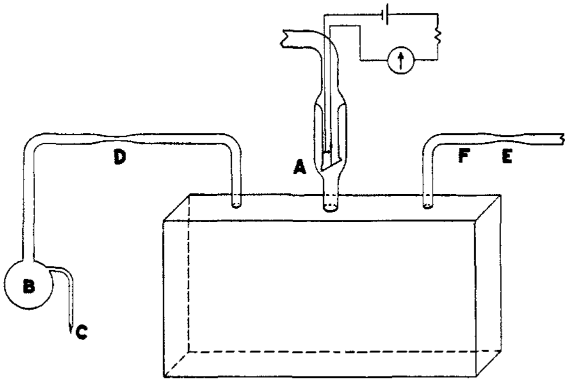

Fig. 1.—Quartz cell for photolysis of gases.

The total volume of the cell including the housing for the diaphragm was 60.3 cc., varying somewhat with the length of the sealed-off connections.

The thermopile of copper–constantan junctions had 26 receivers, 12 × 2 mm. and 0.025 mm. in thickness, which intercepted all the light passing through the cell. It was mounted in a large aluminum casing and set in the thermostat on a vertical track. All cemented parts were made with "Duco" cement which permitted the thermopile to be used over a wide range of temperature, 0 to 60° in the present work. A description of the thermopile and its calibration will be given elsewhere. The reference standard was a radiation lamp, No. 132, from the Bureau of Standards. The thermopile deflection was 6% less at 57° than at 25°.

The acetone was purified by crystallization with sodium iodide, as recommended by Shipsey and Werner,[8] dried, and distilled from calcium chloride. This purified acetone was used throughout, but additional experiments showed that ordinary C. P. acetone gave the same green fluorescence and practically the same results.

Procedure

Before each of the later determinations the cell was rinsed several times with acetone. Water was never used. Dry air was drawn through while the cell was heated

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(7) Daniels, THIS JOURNAL, **50**, 1115 (1928).

(8) Shipsey and Werner, *J. Chem. Soc.*, **103**, 1255 (1913).

with a Bunsen burner. After cooling, the dry, purified acetone was introduced into bulb B through capillary C (Fig. 1). The capillary was sealed off and the bulb immersed in a bath at about −20°. The acetone was evaporated until 0.2 to 0.4 cc. remained, and the cell was then sealed off at E. The entire cell was next immersed in a bath at about 56°, thus giving about one atmosphere's pressure and ensuring the absence of the liquid phase. Lower temperatures were used for lower pressures. The cell and bulb were again cooled in ice while the tube was sealed off at D. This chilling was necessary to reduce the pressure of acetone and prevent a heavy deposit of carbon where the quartz was heated to fusion. Such a deposit not only introduces an impurity but it renders the sealing difficult on account of increased radiation.

When a foreign gas was introduced with the acetone the technique was more complicated because it was necessary to exclude every trace of moisture. Nitrogen or other gas was dried by passage through towers of phosphorus pentoxide and sealed off with fused calcium chloride in a Pyrex bulb of 10-cc. capacity provided with a bent, thin-walled capillary. The bulb was placed in a larger quartz tube 15 cm. long and 1.5 cm. in diameter, sealed onto the cell at F. The cell and tube were filled with acetone vapor and tested for the absence of water. If a normal pressure increase was observed during a short exposure the whole apparatus was then removed from the thermostat and shaken violently to break the small bulb and release the foreign gas. The cell was again chilled and the side arm sealed off.

The cell was immersed in ice and water before and after the photochemical exposure in order to determine, respectively, the vapor pressure of the liquid acetone and the pressure of permanent gases produced by the photolysis. The zero point of the diaphragm was altered by a change in temperature and it was necessary to wait a few minutes to establish stable equilibrium.

In carrying out the photochemical measurements the thermopile–galvanometer readings were taken every fifteen or thirty minutes with both cell and "dummy." The difference between the two readings gave a measure of the energy absorbed by the acetone vapor. An isolated dynamo[9] gave a constant potential of 500 volts and ensured constancy of radiation from the mercury lamp.

Calculations

The following data of a typical determination give the method of calculation.

In this experiment during the exposure of five hours and ten minutes at 56.5° the pressure actually decreased by 3.32 mm. However, when the cell was set in an ice-bath and the acetone was liquefied, the pressure was 17.9 mm. greater than the vapor pressure of the acetone. The condensation products dissolve in the drop of liquid acetone condensing out and give no detectable vapor pressure but the decomposition products do not dissolve in appreciable quantities.

The decomposition is assumed for the purpose of calculation to be represented by the equation

$$(CH_3)_2CO + h\nu = (CH_3)_2CO^* = C_2H_6 + CO$$

so that half the volume increase is a measure of the acetone molecules decomposed. The condensation reaction is assumed to be

$$(CH_3)_2CO^* + (CH_3)_2CO = [(CH_3)_2CO]_2.$$

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[9] The authors are indebted to the Research Committee of the University of Wisconsin for the purchase of this dynamo.

TABLE I

TYPICAL CALCULATION

Temperature	56.5°
Initial pressure	728.8 mm.
ΔP corrected to 0°	−3.32 mm.
Pressure non-condensable gas (0°)	17.9 mm.
Volume of cell	60.3 cc.
Total time of exposure	18,600 sec.
Wave length	3130 Å.
Average galvanometer deflection, control	106.9 cm.
Average galvanometer deflection, cell	7.5 cm.
Radiation absorbed (corrected)	84,000 ergs/sec.

$$\frac{17.9/2}{760} \times \frac{60.3}{22{,}400} \times 6.06 \times 10^{23} = 1.92 \times 10^{19} \text{ molecules acetone decomposed}$$

$$\frac{3.32 + 17.9/2}{760} \times \frac{60.3}{22{,}400} \times 6.06 \times 10^{23} = 2.63 \times 10^{19} \text{ molecules acetone condensed}$$

Total molecules reacting 4.55×10^{19}

Total number of quanta 2.48×10^{20}

$\Phi = 0.18$ molecules per quantum

Each activated molecule that takes part in the condensation causes the shrinkage in volume from two molecules to one molecule. If the pressure remains unchanged during exposure the condensation must be exactly equal to the decomposition (17.9/2 in the example given). To this quantity must be added the actual shrinkage if there is any (3.32 mm.). The activated molecules decomposing and condensing are then added together to give the total number of molecules reacting, photochemically. This number divided by the number of quanta absorbed, after correcting for transmission and reflection, gives Φ the quantum yield.

Experimental Results

Absorption of Light.—Absorption spectra were obtained for acetone vapor using a hydrogen tube. Absorption was complete to 3200 Å. and partial to 3400 Å. At the low dispersion obtained with a quartz prism and 20-cm. plate there was no evidence of discontinuity or line structure in the absorption.

The absorption of monochromatic light by gaseous acetone followed Beer's law with exactness—a fact which increases confidence in the purity of the light and in the simple nature of the absorption process. The ratio of the thermopile–galvanometer deflections with acetone vapor to the deflections with the control cell gave directly the percentage absorption. Measurements were made at ten different pressures and an excellent straight line was produced by plotting the logarithm of the transmission against the pressure. The absorption coefficient k, defined by the equation $I = I_0e^{-kcl}$, where I represents intensity and c represents concentration in moles per liter, has an average value of 6.63 ± 0.06 at 3130 Å.

and 25.9 ± 0.4 at 2650 Å. The length l is expressed in cm. These values are in good agreement with those of Porter and Iddings.[3]

Quantum Yield.—The number of molecules reacting per quantum absorbed is given in Table II for radiation of 3130 Å. and at pressures near atmospheric.

TABLE II

THE QUANTUM EFFICIENCY OF GASEOUS ACETONE AT 3130 Å.

Total pressure, mm.	633.2	684.2	742.2	768.6	766.3	760.0	732.7	733.4
Intensity, ergs per second	35,500	41,000	64,600	63,600	44,000	85,200	66,800	84,000
Total time, seconds	50,300	74,800	27,000	19,800	25,000	23,000	16,000	18,600
ΔP in mm. 56°	10.0	−1.8	31.4	12.5	16.9	30.4	−1.9	−4.0
ΔP in mm. 0°	27.0	34.3	28.6	21.6	22.4	24.7	16.3	17.9
Molecules decomposed $\times 10^{-19}$	2.86	3.62	5.47	2.27	2.93	5.28	1.76	1.92
Molecules condensed $\times 10^{-19}$	1.11	3.95	3.00	0.1	None	None	2.08	2.63
Molecules per quantum, Φ	0.17	0.16	0.20	0.12	0.17	0.17	0.23	0.18

Average 0.17 ± 0.02 (average deviation from the average)

The intensity is given in ergs per second absorbed by the acetone vapor. The cross section of the beam of light passing through the cell was approximately 1.5 × 30 mm., so that the energy absorbed per sq. mm. of cell frontage may be obtained by dividing the given intensity by 45. The quantum efficiency is calculated on the basis of total number of molecules of acetone reacting regardless of the final product. As explained before the decomposition reaction is measured by ΔP at 0° in the presence of liquid acetone and the condensation reaction, catalyzed by traces of water, is measured by this value together with the ΔP obtained in the gas phase at 56°. It will be noticed that at 56° the value of ΔP varies greatly and is sometimes positive and sometimes negative. It would be impossible to draw any conclusions regarding quantum yields from these data alone. The close checks obtained in the last line are very satisfactory, however, and support the theoretical foundations on which the calculations are based. The quantum efficiency decreases markedly at low pressures as shown in Table III.

TABLE III

EFFECT OF PRESSURE ON THE QUANTUM YIELD AT 3130 Å.

Total pressure, mm.	53.9	84.2	366.6	387.2
Intensity, ergs per second	26,200	20,500	11,600	51,000
Time in seconds	28,000	35,000	18,000	19,000
ΔP in mm.	2.52	2.70	3.2	5.6
Molecules decomposed $\times 10^{-19}$	0.437	0.468	0.557	1.23
Molecules condensed $\times 10^{-19}$	None	None	None	0.255
Molecules per quantum	0.04	0.04	0.17	.10

These results are less accurate than those in Table II because the lessened absorption leads to smaller changes. In three of the experiments there was no condensation. The value 0.17 in the third experiment is not significant because the intensity was inadvertently decreased materially, thus changing two variables at a time. The value of Φ at one-tenth atmosphere is roughly one quarter the value at atmospheric pressure and according to a limited number of experiments the value at half an atmosphere is about two-thirds.

The quantum yield is increased by decreasing the intensity of light as shown by comparing Table IV with Tables II and III. The intensities are so low and the changes in pressure so small that the percentage error is large, but it is evident that a reduction in intensity to about one-tenth has increased the quantum yield by more than 50%.

TABLE IV

QUANTUM YIELD AT LOW INTENSITIES AND 3130 Å.

Total pressure, mm.	673.7	433.0	425.1	742.3	723.2	696.2	772.8	762.8
Intensity, ergs per second	5440	5950	5360	5160	2100	3200	5070	3330
Time in seconds	50,080	20,500	20,000	29,000	13,000	40,000	34,000	44,000
ΔP in mm.	2.5	2.2	3.0	3.7	0.5	2.0	4.9	5.2
Molecules decomposed $\times 10^{-19}$	1.08	0.389	0.524	0.645	0.090	0.347	0.850	0.900
Molecules condensed $\times 10^{-19}$	0.645	None	None	None	None	None	None	None
Molecules per quantum	0.40	0.20	0.30	0.27	0.28	0.17	0.31	0.38

Average 0.29 ± 0.06

The quantum yield at two different wave lengths in the absorption region is the same as shown by comparing the data of Table V at 2650 Å. with those in Table IV at 3130 Å. The values at 2650 Å. must be compared with the low intensity values of Table IV because it was impossible to obtain high intensities at this wave length. Porter and Iddings[3] by an indirect method concluded also that the quantum yield is independent of the magnitude of the quantum.

TABLE V

QUANTUM YIELD AT 2650 Å.

Total pressure, mm.	711.6	717.0	693.0
Intensity, ergs per second	8630	7970	6380
Time in seconds	23,400	22,020	25,200
ΔP in mm. (56°)	6.2	3.8	4.0
Molecules decomposed $\times 10^{-19}$	1.08	0.662	0.697
Molecules condensed $\times 10^{-19}$	None	None	None
Molecules per quantum	0.39	0.28	0.32

Average 0.33

In order to prove that there is no dark reaction, acetone vapor was sealed off in the quartz cell and maintained continuously at 55.8° for a period longer than the photochemical experiment. In one experiment with dry acetone the pressure registered exactly 755.0 mm. for a period of fourteen hours. In another experiment with acetone containing a trace of water, as shown by a decreasing pressure in the photochemical experiment, there was no significant change of pressure (increase of 0.6 mm.) over a period of forty-two hours.

Effect of Water.—In the earlier experiments an actual decrease in pressure rather than an increase was often produced by the absorption of ultraviolet light. This fact could not be explained by decomposition; some type of condensation reaction was obviously occurring. It became evident that the condensation was lessened by extra precautions in eliminating traces of water. The ratio of molecules condensed to molecules decomposed was determined from the pressures determined in the presence and absence of liquid acetone, as explained before. In four experiments the liquid acetone contained water, as shown by a blue color produced with anhydrous copper sulfate. In these experiments the ratio of molecules condensed to molecules decomposed was, respectively, 0.92, 0.80, 1.18 and 1.37, while in two others where special precautions had been taken to eliminate moisture there was no condensation whatever.

In another experiment it was found that the addition of 1×10^{17} molecules of water, giving a partial pressure of 0.04 mm., caused 1.15×10^{19} molecules to undergo the photo-condensation reaction while 1.43×10^{19} molecules were undergoing photo-decomposition. The water was introduced by breaking a bulb, containing nitrogen saturated with water at 0°, in a side tube as already described. It was first established by the absence of any photo-condensation reaction that the original acetone vapor was dry.

Other gases were tested in a similar manner with this same all-quartz technique and it was found that the addition of 15 to 25 mm. of dry nitrogen, hydrogen or carbon monoxide does not cause any photo-condensation whatever.[10]

Reaction Products.—In order to obtain enough gaseous products to analyze, the slits of the monochromator were opened wider and the photolysis was continued for thirty hours. The cell was cooled with carbon dioxide snow and the permanent gases were pumped out with a modified Sprengel pump. In one determination 1.55 cc. was obtained and in another 2.15 cc. These gases contained no unsaturated hydrocarbons, as proved by bromine water. The average gas analysis as determined by slow combustion in a Burrell–Haldane apparatus was CO, 51.1, C_2H_6, 38.8 and H_2, 10.0%. The analyses did not include the determination of methane. The results are in good agreement with those reported by Kirkbride and Norrish[11] and by Berthelot and Gaudechon.[12]

To obtain more material for analysis the monochromator was temporarily discarded and the capillary lamp operating on 750 watts was placed at the center of a double-walled cylindrical quartz cell, provided with a reservoir of boiling acetone and a reflux condenser. A Pyrex tube around the water-cooled lamp filtered out all radiation below 3130 Å. Before starting an experiment the acetone was cooled and the whole system was subjected to continued evacuation to remove air. Permanent gases were evolved at the rate of 150 cc. per hour and analyzed with a Burrell gas analysis apparatus. The analyses are summarized in Table VI.

TABLE VI

ANALYSIS OF GASES PRODUCED BY PHOTOLYSIS

	CO_2	CO	H_2	C_2H_6	CH_4	Total
Dry acetone (average)	3.6	47.0	4.2	27.9	13.2	96.0
Acetone + water	1.1	49.1	4.3	30.1	14.5	99.1
Diacetone alcohol	0	49.4	4.3	30.4	14.2	98.3

Carbon dioxide and carbon monoxide were obtained by direct absorption, hydrogen was obtained by slow combustion over copper oxide and ethane and methane by slow combustion. Ethane and methane was the only combination of paraffin hydrocarbons which could give the combustion data obtained. The study of the products of photolysis is being extended in this Laboratory.

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(10) Twelve earlier experiments, in which these gases were thoroughly dried and introduced into the cell through a stopcock and then sealed off, showed considerable photo-condensation. These misleading data might have been accepted except for the fact that carbon monoxide produced in the photochemical decomposition had no effect. When the stopcock was eliminated the effect disappeared. The extent of the photo-condensation was about the same as that produced by one micromole of water. These facts are recorded merely to emphasize the limitations of stopcocks.

(11) Kirkbride and Norrish, *Trans. Faraday Soc.*, **123**, 407 (1931).

(12) Berthelot and Gaudechon, *Compt. rend.*, **155**, 207 (1912).

The liquid acetone, condensed after an experiment, was always straw yellow or brownish depending on the length of exposure. The color was probably due to colloidal carbon. There was very little residue after the acetone was boiled away. This result was rather unexpected in the case of acetone to which water had been added, for the experiments using the monochromator showed that under these conditions a condensation reaction predominated.

The difference between the monochromator experiments and the filter experiments is probably due to the fact that in the latter case radiation of 3650 Å. was present as well as radiation of 3130 Å. Acetone is transparent to 3650 Å. and it might be supposed that this wave length would be entirely without effect, and that the filter technique would be just as effective as the monochromator. However, in the cylindrical cell with both 3130 and 3650 Å. there was no observed condensation reaction and no difference in the rate of evolution of permanent gases when water was added to the acetone, although a difference would be expected on the basis of the monochromator experiments. The photolysis of pure diacetone alcohol was studied because this material is thought to be the product of the condensation reaction which is catalyzed by water. It was found that diacetone alcohol absorbs light of 3650 Å. nearly as completely as light of 3130 Å., and that light of 4050 and 4360 Å. is only slightly absorbed. As shown in Table VI, exposure to ultraviolet light gives exactly the same products with diacetone alcohol as with acetone. It seems likely then that diacetone alcohol is produced by photolysis of moist acetone but that it in turn is decomposed to permanent gases by light of 3650 Å. which is present in large amounts in the filter technique. This light is absent in the monochromator experiments where the condensation is observed. Such a situation justifies the use of the monochromator and shows that erroneous conclusions may be drawn when working with radiation that is not monochromatic, even in comparatively simple cases.

It must be emphasized that no direct test was obtained for diacetone alcohol in the products of photolysis. Absorption spectra and boiling point data gave negative results but the intensity of light was very low in the monochromator experiments; and any diacetone alcohol formed in the filter experiments was decomposed by light of other wave lengths.

Fluorescence.—The irradiation of acetone vapor (dry or moist) always produced a bright green fluorescence. If any oxygen was present, however, the fluorescence was blue. In the later experiments with adequate evacuation the vapor showed the green fluorescence instantly as soon as the ultraviolet light was introduced. In the earlier experiments the color was first blue and the sharp change to green came after a time depending on the amount of oxygen present. The photo-oxidation accompanied by the blue fluorescence results in a decrease of pressure. In one case where there was a large amount of air the blue fluorescence lasted for 372 minutes, and the pressure decreased 19.6 mm. The transition to green occupied one minute and a further exposure of 150 minutes caused an increase in pressure of 0.3 mm. The sudden change in color evidently comes when the oxygen is entirely used up, and the color line between blue and green can be seen to move steadily through the cell from front to back. In one experiment the transition from all blue to all green occupied forty seconds and since energy (3130 Å.) was being absorbed at the rate of 56,000 ergs per second the change involved the absorption of 3.6×10^{17} quanta. *Assuming* that the quantum efficiency is the same for oxidation (0.2 molecule per quantum) as for decomposition and that not over 2 molecules of oxygen are involved in the oxidation of acetone, one may calculate that these 3.6×10^{17} quanta correspond to 1×10^{17} molecules of oxygen or to a partial pressure of 0.03 mm. If a chain reaction is involved the value will be larger. It is possible that this green fluorescence of acetone vapor may be used as a simple, sensitive test for the absence of traces of oxygen.

The fluorescence was independent of the wave length absorbed (3130 Å. and below). Diacetone alcohol showed green fluorescence at 3650, 4050 and 4360 Å. but only slight fluorescence at 3130 Å. and below.

The nature of the fluorescence was studied further by photography. The exciting line was monochromatic light of 3130 Å. from the capillary lamp and monochromator. Green fluorescence was obtained by introducing 5 cc. of acetone into a quartz cell, evaporating most of it with an oil pump, chilling in carbon dioxide snow and sealing off. Blue fluorescence was obtained by using an ordinary cork, which allowed some access of air. The collimator of the spectrograph was placed at right angles to the exciting beam from the monochromator. Eastman Seed panchromatic plates were used. The liquid acetone gave a vapor pressure of about 250 mm. and the absorption was about 11%.

The green fluorescence is much more intense than the blue, an exposure of one hour with the former giving a more dense plate than six hours with the latter. The spectrograms were analyzed with a Moll recording microphotometer. The green fluorescence showed two maxima: one extending from about 4100 to 4820 (maximum at 4580); the other from 4990 to the limit of plate sensitivity 5210 Å. Careful visual inspection in the spectrograph failed to reveal any fine structure in the green band. The six-hour exposure to the blue fluorescence showed a continuous region extending approximately from 4030 to 4720 with a maximum near 4340 Å.

Although it was not possible to determine the intensity of fluorescence, an estimate of an upper limit was necessary for proper interpretation of the quantum yield. The large thermopile was placed at the side of the rectangular cell where it absorbed approximately 7% of the total radiation emitted from the cell. The scattered light was more intense than the fluorescent light as shown by the fact that the empty cell gave practically the same deflection as the cell filled with acetone vapor. The sensitivity of the measurement was low but it was possible to estimate an upper limit. The fluorescent light could not have been over 3% of the radiation absorbed, and it may have been much less than 3%.

Theoretical Discussion

When a molecule of gaseous acetone absorbs a quantum of ultraviolet light, it becomes activated by electronic displacement, and may then (1) react chemically, (2) emit fluorescent light, or (3) transmit extra translational energy to the molecules with which it collides. The experimental facts recorded show that under certain conditions the chances are, respectively, about 17 in 100 for chemical reaction; less than 3 for fluorescence; and 80 for degradation as heat. The low chemical yield cannot be attributed to fluorescence. Apparently the electronic energy does not easily become localized in the type of vibrational energy of the atoms, which leads to disruption or chemical action. Collisions with other molecules, rather specific in nature, are necessary to effect this localization of energy which is a necessary step preceding the chemical reaction. For every fruitful collision, however, there are many collisions which do not lead to chemical action and these unfruitful collisions merely carry away a little of the energy in the form of increased kinetic energy, *i. e.*, raise the temperature. Experimental evidence for this view is found in the fact that the pressure of the cell often decreased by a millimeter or less when the illuminating beam was turned off. The relation of the time between collisions to the time required to localize the energy in a given part of the molecule is a matter of theoretical interest.

Decreasing the pressure from one atmosphere to one-tenth of an atmosphere decreases the quantum yield from about 0.17 to approximately 0.04 molecule per quantum and decreasing the intensity of radiation to one-tenth nearly doubles the yield. The two effects seem to be related. An activated molecule has a better chance to react chemically when it is surrounded by a large excess of inactive molecules.

The energy required to activate a mole of acetone for thermal decomposition is 68,500 calories.[13] Radiation of 3130 Å. (91,100 calories per mole) and 2650 Å. (107,500 cal.) is ample for decomposition assuming that the photochemical decomposition has the same mechanism as the thermal decomposition. When green light (53,800 cal.) is emitted as fluorescence, the excited molecules have insufficient energy left for decomposition. Fluorescence, however, appears to be a comparatively unimportant factor in the chemical reaction. There is no evidence of secondary reactions or chain reactions which complicate many photochemical reactions.

Little can be said regarding the fluorescence. Fine structure in the

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(13) Hinshelwood and Hutchinson, *Proc. Roy. Soc.* (London), **A111**, 245 (1926).

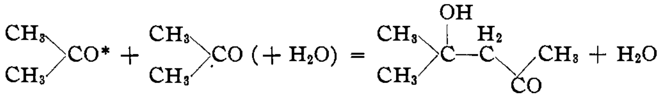
absorption band would naturally be associated with fluorescence. Although there is no record of such fine structure now available it is possible that it may sometime be found. The blue fluorescence involves photo-oxidation, for as soon as the oxygen is consumed the fluorescence changes to green. The accompanying shrinkage in volume shows that a complex oxidation product is formed and that the oxidation does not go to carbon dioxide and water. The spectrographic study shows that even in the absence of oxygen the fluorescence contains some blue which is masked to the eye by the more intense green. It is possible that the oxidation reaction instead of producing a blue fluorescence merely quenches the green and permits the blue to become evident.

The analysis of the decomposition products seems to indicate that every activated molecule which decomposes does so by splitting out the CO group as carbon monoxide. The two remaining CH_3 groups then combine and form ethane more than half of the time but they also combine to give methane, free carbon and hydrogen. It was thought that a secondary photochemical reaction of the ethane, produced by the decomposition of acetone, might account for the methane and other products. To check this possibility the cell 10 cm. in length was filled with purified ethane at 750 mm. pressure and measured with the monochromator. At 3130 Å. only 6% of the light was absorbed and at 2650 Å., 9%. This small absorption might have been due to residual impurities but at least the absorption is so slight that it can be neglected entirely in the photolysis of acetone where the pressure of ethane would be only a few millimeters.

It is well known that polychromatic light frequently leads to a variety of chemical products but any hope that monochromatic light must give only one set of products is shown by these facts to be unwarranted.

The condensation reaction produced by water vapor is interesting. The water acts as a catalyst without being used up in the reaction, as shown by the experiment in which 1×10^{17} molecules of water caused 2.3×10^{19} molecules of acetone to undergo the condensation reaction. The rate of condensation was just as rapid at the end of the experiment, which lasted four hours, as at the beginning. No stoichiometrical relation involving water is possible.

The most likely reaction appears to be the formation of diacetone alcohol according to the equation



$$(CH_3)_2CO^* + (CH_3)_2CO\ (+ H_2O) = (CH_3)_2\overset{OH}{C}-\overset{H_2}{C}-CO-CH_3 + H_2O$$

The evidence for this reaction is indirect. It is certain that when a trace of water vapor is present two molecules of acetone vapor condense to give one molecule of some new gaseous substance and that this substance is absorbed in liquid acetone. It was on this basis that the quantum calculations were made; and the resulting uniform values of Φ shown in Table II could not have come fortuitously from the mass of discordant pressure changes (sometimes positive and sometimes negative) unless these assumptions were correct. Furthermore, the constancy of Φ shows that the decomposition and condensation reactions have the same quantum efficiency. This reaction is supported also by the fact that the condensation reaction was not observed when light of 3650 Å. was present. This light is absorbed by diacetone alcohol but not by acetone, and when it is absorbed the products of photodecomposition are the same as those of acetone. Furthermore, it is known that acetone may be converted into diacetone alcohol by several different catalysts, including water.[14]

This gaseous reaction, which is effected by simultaneously adding water molecules and energy to acetone molecules, may be helpful in studying related problems. Water alone produces no change as proved by the absence of a dark reaction; and energy alone leads to decomposition rather than to the formation of the condensation product.

In forming a molecule of diacetone alcohol it appears necessary to have simultaneously in contact a molecule of water and two molecules of acetone, one of which must be activated. Such a condition may be effected by a triple collision or by a bimolecular collision giving a temporary complex (sticky collision) followed by another bimolecular collision. Several mechanisms are possible. If the collision between the activated and unactivated acetone molecules results in a delayed decomposition the double molecule may be hit by a water molecule changing the type of vibration so as to give diacetone alcohol. More likely, perhaps, is a sticky collision between a normal acetone molecule and a water molecule followed by collision with an activated molecule. It is known that acetone and water tend to form a complex in the liquid state and it is likely that the water may cause a shift to the enol configuration. The third possibility in successive bimolecular collisions, that of collision between an activated acetone molecule and a water molecule followed later by collision with an unactivated acetone molecule, seems less probable.

The triple collision mechanism appears to be possible. In one experiment the concentration of normal acetone molecules was 2.2×10^{19} per cc., the concentration of water molecules necessary to give the condensation reaction was 1.7×10^{15} per cc., the volume of the illuminating beam of light was 4.5 cc. and the number of activated molecules of acetone produced (equal to the number of quanta absorbed) per second was 1.33×10^{16}. If it is assumed that the life of an activated molecule is 10^{-7} second and that the distance between molecules necessary for chemical reaction is 10^{-7} cm., the standard formula[15] gives 2.2×10^{15} triple collisions per

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[14] Dawson, *Trans. Faraday Soc.*, **24**, 640 (1928).

[15] Tolman, "Statistical Mechanics with Applications to Physics and Chemistry," The Chemical Catalog Co., New York, 1927, p. 248.

second. In the experiment from which the data were taken, 0.7×10^{15} molecules of condensation product (probably diacetone alcohol) were produced per second. Although the estimates of the life of an activated molecule and the distance necessary for chemical reaction are very uncertain, the number of triple collisions and the number of molecules of condensation product are at least of the same order of magnitude.

Summary

1. Apparatus for measuring quantitatively the photolysis of gases is described.
2. The quantum efficiency in gaseous acetone was found to be 0.17 molecule per quantum at atmospheric pressure and 56° when the incident light was over 100,000 ergs per sq. cm. per sec.
3. The quantum efficiency increases at low intensities, decreases at low pressures, and remains independent of wave length between 3130 and 2650 Å.
4. Acetone vapor gives a green fluorescence. A trace of oxygen changes it to blue. The energy of fluorescence is less (perhaps much less) than three per cent. of the energy absorbed.
5. Acetone, when dry, is decomposed by ultraviolet light into carbon monoxide, ethane, methane and hydrogen. Carbon monoxide constitutes half of the gaseous products.
6. Diacetone alcohol yields the same products of photolysis as acetone.
7. A trace of moisture catalyzes a photo condensation reaction. The product is probably diacetone alcohol.
8. The quantum efficiency is the same for the condensation reaction as for decomposition.
9. Possible mechanisms for the reactions are discussed.

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