

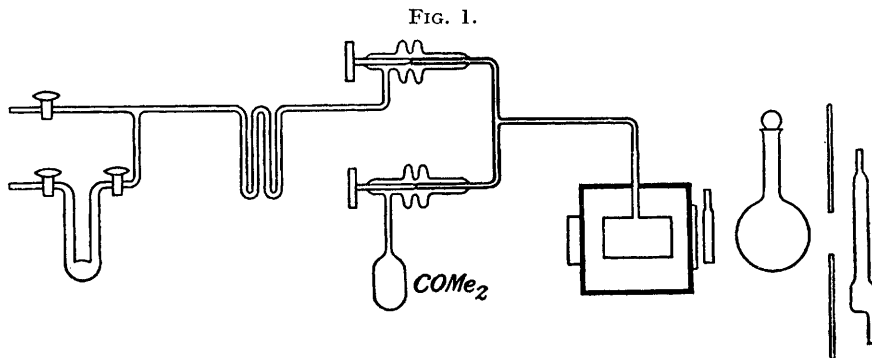
71. *The Photo-decomposition of Gaseous Acetone.*

By ROBERT SPENCE and WILLIAM WILD.

It was shown in an investigation of the photo-decomposition of methyl iodide, alone and in the presence of hydrogen (*Proc. Leeds Phil. Soc.*, 1936, **3**, 141), that the probability of reaction occurring between methyl and hydrogen is less than one in  $10^4$  collisions at  $0^\circ$ . Further experiments have been carried out with acetone instead of methyl iodide, since acetone is supposed to dissociate in the following manner on absorption of ultra-violet light (Norrish, Crone, and Saltmarsh, J., 1934, 1456):  $(\text{CH}_3)_2\text{CO} + h\nu = 2\text{CH}_3 + \text{CO}$ , and might be expected to yield a higher concentration of methyl than could be obtained from methyl iodide under the same conditions of illumination. According to Norrish *et al.* (*loc. cit.*), the ultimate products of the decomposition of acetone are ethane and carbon monoxide in equal volume. However, our initial experiments in the presence of hydrogen always gave  $\text{C}_2\text{H}_6/\text{CO} = 3/2$ . Experiments with pure acetone gave the same result, and furthermore, it was found that diacetyl is formed in considerable amount at room temperatures (Spence and Wild, *Nature*, 1936, **138**, 206). A detailed analytical study of the photo-decomposition was therefore undertaken in order to discover the cause of the discrepancy. The analytical results of previous workers are not entirely consistent, and it seems probable that the composition of the products depends largely on the experimental conditions, a conclusion which is fully in agreement with our own experiments.

## EXPERIMENTAL.

Acetone (B.D.H. *ex* sodium iodide) was fractionated, and individual samples were dried with calcium chloride, magnesium perchlorate, and phosphoric oxide. Further treatment with



sodium iodide and drying agents produced no change in the final results. Acetone thus prepared had the correct b. p. and vapour pressure. The final fractionation was carried out in a vacuum in an all-glass apparatus free from stop-cocks, and the experimental sample was sealed off while frozen in liquid air.

The apparatus was constructed as shown in Fig. 1. A cylindrical quartz reaction vessel, 7 cm. in length and with plane windows 4 cm. in diameter, was connected to the rest of the apparatus by means of a graded seal. It was contained in a substantial aluminium casting to obviate large fluctuations of temperature. The total volume of the reaction system was 77.7 c.c. In order to avoid the effects due to extraneous moisture (Damon and Daniels, *J. Amer. Chem. Soc.*, 1933, **55**, 2365), direct connections to the reaction vessel were made through greaseless Pyrex-glass valves (Bodenstein, *Z. physikal. Chem.*, 1930, *B*, **7**, 387), and this part of the apparatus was separated from the rest, which contained stop-cocks lubricated with Apiezon grease, by a double U-tube cooled in carbon dioxide-acetone or liquid air. Owing to the large number of experiments and the long duration of each, it was necessary to use three different mercury arcs. These were of the straight pattern, working on the 110-volts supply at about 3 amps. The full light of the arc was condensed into an approximately parallel beam by a quartz flask (300 c.c.) filled with water. A photo-electric cell fixed in a suitable position was used as a check on the light intensity. Uncontrollable fluctuations ( $\pm 15\%$ ), probably due to varying line

voltage, occasionally occurred. Using this system, we have been unable to observe any anomalous effects traceable to moisture, nor was there any detectable difference between the samples of acetone subjected to different degrees of drying. The reaction products were pumped off through a liquid-air trap by a Töpler pump, and the non-condensable gases collected and analysed in a special Bone and Wheeler apparatus suitable for small amounts of gas. The general method of analysis was to test first of all for carbon dioxide and oxygen, although these were never present in any measurable quantity. Carbon monoxide was then determined by absorption in ammoniacal cuprous chloride, and the residual gas was exploded with oxygen. After the contraction had been observed, the carbon dioxide produced was absorbed in alkali, thus providing a check on the methane figure calculated from the contraction. In a number of experiments, however, the amount of methane was too small for an accurate combustion determination to be made. A second gaseous fraction, which proved to be pure ethane, was collected with the trap immersed in solid carbon dioxide-ether. Since ethane is readily soluble in acetone (Horiuti, *Sci. Papers Inst. Phys. Chem. Res. Tokyo*, 1931, 17, 182), the trap was then allowed to warm to room temperature, and again pumped out at  $-78^{\circ}$ . This was repeated until no more gas could be obtained. Ethane was determined from the contraction and from the amount of carbon dioxide produced after explosion with oxygen. The ratio  $C_2H_6/CO$  remained unchanged when the ethane was collected at  $-110^{\circ}$ . Decomposition occurring at room temperatures in the full light of the mercury arc was first studied, an acetone pressure of 160 mm. being used. The results (Table I, a) show that the degree of dryness is without appreciable effect on the reaction. The data marked with an asterisk refer to experiments in which the mercury manometer was omitted from the apparatus and in which special care was taken to free the system from extraneous substances. However, the introduction of a mercury manometer did not affect the results. In experiments with 160 mm. of acetone, the fraction of light absorbed would be large.

TABLE I.

*Photo-decomposition at Room Temperatures with the Full Arc.*(a) *Influence of drying.*

No.	Desiccant.	COMe <sub>2</sub> , mm.	Temp.	Time, hrs.	Products, c.c. at N.T.P.			COMe <sub>2</sub> decomposed.			C <sub>2</sub> H <sub>6</sub> /CO.
					CO.	CH <sub>4</sub> .	C <sub>2</sub> H <sub>6</sub> .	C.c. at N.T.P.	%.	Yield per 10 hrs.	
1	CaCl <sub>2</sub>	160	21.6°	8	1.61	—	2.43	3.25	21.3	4.06	1.51
2	„	156	19.5	24	4.46	0.22	6.54	8.62	57.9	3.60	1.47
3	Mg(ClO <sub>4</sub> ) <sub>2</sub>	164	22.0	14	2.82	—	4.03	5.24	32.8	3.74	1.43
4*	P <sub>2</sub> O <sub>5</sub>	160	20.0	17	3.39	0.11	4.77	6.14	40.3	3.61	1.41
5*	„	160	20.0	17	2.72	—	4.18	5.64	36.2	3.34	1.54
6*	„	160	20.0	17	2.72	—	3.90	5.08	33.3	2.93	1.44
32	CaCl <sub>2</sub>	160	21.0	17	2.17	0.07	3.29	4.41	28.9	2.60	1.52

(b) *Influence of intensity.*

No.	COMe <sub>2</sub> , mm.	Temp.	Time, hrs.	Screen trans- mission, %.	Products, c.c. at N.T.P.		COMe <sub>2</sub> decomposed.			C <sub>2</sub> H <sub>6</sub> /CO.
					CO.	C <sub>2</sub> H <sub>6</sub> .	C.c. at N.T.P.	%.	Yield per 10 hrs.	
55	163	22.0°	17	100	2.13	3.45	4.77	30.7	2.81	1.62
61	163	19.5	2.5	100	0.29	0.47	0.65	4.2	2.60	1.62
62	164	20.5	3	100	0.428	0.683	0.94	6.0	3.13	1.59
58	162	21.0	19	60	1.07	1.88	2.69	17.4	1.42	1.76
54	165	20.5	15	40	0.566	1.04	1.52	9.7	1.01	1.84
56	161	21.0	24	18	0.399	0.789	1.18	7.7	0.49	1.98
57	161	20.0	48	7	0.313	0.586	0.86	5.6	0.19	1.87
60	164	19.0	67	2.5	0.207	0.323	0.44	2.8	0.066	1.56

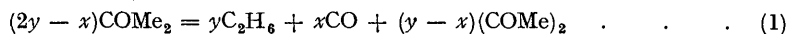
The product remaining in the trap was always yellow. The condensate from 20 successive experiments similar to Nos. 4, 5, and 6 (Table I, a) was therefore collected in a micro-fractional distillation apparatus, which was sealed to the trap. The latter was subsequently cut off and weighed. A sharp separation of unchanged acetone (0.9 g.) from a yellow liquid (0.1 g.) was achieved by immersing the bulb in a beaker of water, the temperature of which was carefully controlled. It is evident that more acetone entered the reaction vessel than the amount calculated from the pressure (0.78 g.), probably owing to the accumulation of a brown, viscous substance (0.03 g.), extremely soluble in acetone, on the cylindrical wall of the reaction vessel. In later experiments, the reaction vessel was cleaned at frequent intervals. The b. p. (micro-

method) of the yellow liquid was 87—88°, identical with that of pure diacetyl, which was determined simultaneously. The following derivatives were prepared.

*Nickel dimethylglyoxime.* One drop of the liquid was added to a solution of hydroxylamine hydrochloride (0.5 g.) in water (1 c.c.) and heated to boiling. The white crystalline precipitate was filtered off, washed with cold distilled water, and dried at 100° (cf. Mulliken, "Identification of Organic Compounds," Vol. 1); m. p. 234—236°, showing no depression on admixture with authentic dimethylglyoxime (m. p. 235°). Addition of a few drops of aqueous nickel sulphate to an aqueous-alcoholic solution of the remaining solid gave a scarlet precipitate of nickel dimethylglyoxime.

*Diacetyl 2 : 4-dinitrophenylhydrazone.* This derivative was prepared by Brady's method (J., 1931, 756). A brown micro-crystalline powder was obtained by recrystallisation from pyridine, and orange leaflets from nitrobenzene, m. p. 336—337°. An authentic sample melted at 337° and the mixed m. p. was the same.

Gas analyses of different experiments in the series gave results similar to those shown in Table I, a. Assuming for purposes of calculation, that 3 vols. of ethane are produced for every 2 vols. of carbon monoxide, we can represent the change stoicheiometrically as follows:  $4(\text{CH}_3)_2\text{CO} = 3\text{C}_2\text{H}_6 + 2\text{CO} + (\text{CH}_3\text{CO})_2$ . The amounts of ethane and carbon monoxide formed would therefore require a yield of 0.105 g. of diacetyl, whereas 0.1 g. was actually obtained. If it is assumed that diacetyl is the sole non-gaseous product, the equation can be written in general form for any  $\text{C}_2\text{H}_6/\text{CO}$  ratio, *viz.*,



The number of c.c. of acetone vapour decomposed per 10 hours has been calculated from the yields of ethane and carbon monoxide with the help of the above equation, and the methane which is produced in a relatively small amount has been disregarded.

*Experiments with Filtered Light.*—Having determined the general course of the reaction occurring in the full light of the mercury arc, we carried out experiments in the same apparatus, using filtered light of different intensities.

*Filter for the continuum.* The quartz flask was filled with a solution of nickel and cobalt sulphates of suitable concentration (Bowen, J., 1935, 76), and used in conjunction with a cylindrical quartz cell (5 cm.  $\times$  5 cm.) containing chlorine gas at 420 mm. pressure. Spectrograms taken with a copper-spark source showed that this combination transmitted radiation between 2200 and 2900 Å., the greater portion being less than 2750 Å. The transmission, which was frequently tested, remained unchanged after long periods of illumination. Different intensities were obtained by interposing calibrated screens of oxidised copper gauze. The results are given in Table II.

TABLE II.

*Photo-decomposition in the Region of Continuous Absorption.*  
*Influence of light intensity and acetone pressure.*

No.	COMe <sub>2</sub> , mm.	Temp. °C.	Time, hrs.	Screen trans- mission, %	Products, c.c. at N.T.P.			COMe <sub>2</sub> decomposed.				
					CO.	CH <sub>4</sub> .	C <sub>2</sub> H <sub>6</sub> .	C.c. at N.T.P.		Yield per 10 hrs.		C <sub>2</sub> H <sub>6</sub> /CO.
36	160	20.0°	48	100	1.69	0.20	4.13	6.56	43	1.37	2.44	
37	160	19.5	21.5	100	0.66	0.06	1.61	2.57	16.9	1.19	2.44	2.44
49	161	21.0	17	100	0.63	0.04	1.55	2.48	16.2	1.46	2.47	2.47
63	160	20.0	21	60	0.422	—	0.921	1.42	9.3	0.68	2.18	2.18
44	160	21.0	25.5	29	0.230	—	0.512	0.794	5.2	0.31	2.23	2.23
39	160	20.0	41	12	0.172	—	0.321	0.469	3.1	0.115	1.87	1.87
46	160	21.0	48	12	0.169	—	0.275	0.381	2.5	0.079	1.63	1.63
40	70	20.0	24	100	0.499	—	0.967	1.44	21.6	0.598	1.94	1.94
43	70	20.0	18	100	0.455	—	0.874	1.29	19.4	0.719	1.92	1.92
42	32	20.0	26	100	0.427	—	0.690	0.953	31.1	0.367	1.62	1.62

The most interesting feature of the experiments with light in the continuum region is associated with the effect of varying intensity. As the light intensity increases from a low value to the highest attainable with the apparatus, the ratio  $\text{C}_2\text{H}_6/\text{CO}$  approaches a maximum value of approximately 2.5, as compared with a value of 1.5 for the full arc. Increase of acetone pressure at constant intensity also appears to increase the ratio. Since the continuum light differs from that of the full arc mainly by lack of light in the banded region of absorption, it was thought that the difference in the ratio  $\text{C}_2\text{H}_6/\text{CO}$  might be due to a low value in the banded

region. The hypothesis was tested by an experimental determination of the ratio in the band region.

*Filters for the band region.* The water filter together with a 1 cm. layer of potassium chromate (0.25 g. per litre) transmitted the line 3130 Å. and some 3020 Å., whilst removing the shorter ultra-violet light and radiation between 3400 and 4360 Å. An attempt was made to employ a filter consisting of a 1-cm. layer of potassium phthalate (0.025*M*), but the amount of decomposition obtained was much less than expected, owing to the instability of the filter.

TABLE III.  
*Photo-decomposition in the Region of Banded Absorption.*

No.	Filter.	COMe <sub>2</sub> , mm.	Temp.	Time, hrs.	Products, c.c. at N.T.P.		COMe <sub>2</sub> decomposed.			
					CO.	C <sub>2</sub> H <sub>6</sub> .	C.c. at N.T.P.	Yield per 10 hrs. %.	C <sub>2</sub> H <sub>6</sub> /CO	
35	Pyrex	160	19.5°	70.5	0.195	0.173	0.184	1.2	0.026	0.89
53	K <sub>2</sub> CrO <sub>4</sub>	164	19.5	48	0.283	0.336	0.389	2.5	0.081	1.19
65	"	164	20.5	46	0.235	0.282	0.325	2.1	0.072	1.20
50	Phthalate	161	20.5	24	0.078	0.078	0.078	0.5	0.033	1.00

Whilst the C<sub>2</sub>H<sub>6</sub>/CO ratio for the banded region is undoubtedly about unity and much lower than the corresponding ratio for the same rate of decomposition in the continuum, the amount of decomposition is much too small to account for the different values obtained in the full arc and in the region of continuous absorption.

*Further experiments with unfiltered light.* In order that the conditions governing the value of the ratio C<sub>2</sub>H<sub>6</sub>/CO might be fully explored, another series of experiments with the full arc was carried out (Table I, *b*). The acetone pressure was maintained constant at 160 mm., and the intensity was systematically reduced by calibrated wire screens of oxidised gauze. The ratio showed a remarkable variation with decrease of light intensity, first increasing to a value of about 2, and then decreasing in the same manner as with the continuum light.

*Influence of Temperature on the Photo-decomposition.*—Previous investigators (Norrish *et al.*; Damon and Daniels, *loc. cit.*) have usually worked at 60°. We have carefully repeated the experiments at this temperature, using the technique developed by Norrish *et al.* (*loc. cit.*), which appears to be most suitable. Acetone, dried over phosphoric oxide or calcium chloride, was distilled into a quartz bulb (200 c.c.) provided with a side tube, which had been thoroughly baked out in a vacuum. Greased stop-cocks were separated from the apparatus by the folded trap (Fig. 1), during evacuation, after which it was sealed off so that acetone came into contact only with Pyrex glass or quartz during the distillation. When 1 c.c. had collected in the side tube, the bulb was sealed off and placed in a double-walled air-thermostat provided with quartz windows and heated by a stream of air passing through an external heater, as described by Norrish. The wave-length of the light was regulated by filters, and the intensity by wire screens. After illumination, the bulb was removed and attached by rubber pressure-tubing to a U-tube immersed in liquid air, which was connected through a stop-cock to a Töpler pump. The trap was evacuated and allowed to stand for several hours to ensure that no leakage occurred at the rubber connexion, after which the fine capillary seal of the quartz bulb was broken and the gases pumped off. The side limb of the quartz bulb was at first maintained at -78°, and then the acetone was allowed to distil slowly into the trap. A second gaseous fraction was obtained when the temperature of the trap was raised to -110°. It was found later that the gas had the same composition if pumped off at -78°. Analytical results are given in Table IV. The light intensity used by Norrish, as determined from the carbon monoxide yield, was

TABLE IV.  
*Photo-decomposition at 60°: influence of intensity (COMe<sub>2</sub> = 860 mm.).*

No.	Radiation.	Time, hrs.	Screen trans- mission, %.	Gaseous products.			
				C.c. at N.T.P.	CO, %.	C <sub>2</sub> H <sub>6</sub> , %.	CH <sub>4</sub> , %.
24	Full arc	9.5	100	13.52	45.0	41.4	13.6
26	Continuum	24	100	4.15	48.3	33.3	18.4
27	"	20	100	3.27	47.6	32.6	19.8
30	"	24	29	1.54	52.6	19.6	27.8
28	"	15	22	0.73	55.0	18.9	26.0
31	None	24	—	0.00	—	—	—

very similar to that in Expt. 30. The acetone remaining in the trap was always colourless, and no evidence of diacetyl formation at 60° could be obtained.

Owing to the high acetone pressures used in the above experiments (*ca.* 860 mm.), the results cannot be directly compared with those obtained at room temperatures. Accordingly, photolyses were performed at 0° and 51° with acetone pressures of 66 mm. and 80 mm. respectively, so that the fraction of light absorbed should be about the same as in the 70 mm. experiments at room temperatures. Since the vapour pressure at 0° is about 70 mm., higher pressures were precluded. The cylindrical quartz cell previously described was placed in a large, well-lagged, tin box. The end window of the cell was attached by sealing wax to a brass tube 5 cm. long, which passed through the side of the box. A few pieces of silica gel were placed in the tube to prevent the window's becoming fogged, and the cylindrical chlorine filter was waxed to the outer end, thus leaving an air-tight, dry space between the filter and the reaction vessel. The box was filled with an ice-water mixture for the experiments at 0°, and fitted with the usual water-thermostat devices for the experiments at 51°. The results are given in Table V, together with the room-temperature data at 70 mm. pressure for purposes of comparison.

TABLE V.  
*Influence of Temperature in the Region of Continuous Absorption.*

No.	COMe <sub>2</sub> , mm.	Temp.	Time, hrs.	Products, c.c. at N.T.P.*		COMe <sub>2</sub> decomposed.			
				CO.	C <sub>2</sub> H <sub>6</sub> .	C.c. at N.T.P.	%.	Yield per 10 hrs.	C <sub>2</sub> H <sub>6</sub> /CO.
67	67.0	0.0°	22	0.265	0.627	0.989	14.4	0.45	2.37
68	66.5	0.0	22	0.230	0.516	0.802	11.7	0.37	2.24
40	70	20	24	0.499	0.967	1.44	21.6	0.60	1.94
43	70	20	18	0.455	0.874	1.29	19.4	0.72	1.92
69	80	51	18	0.540	0.615	0.69	10.0	0.38	1.14
70	83	51	18	0.459	0.495	0.53	7.4	0.30	1.08

\* The methane formed in these experiments never constituted more than 5% of the total gaseous products.

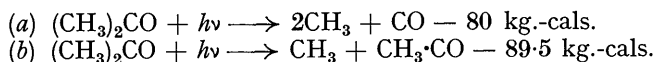
The experiments at 0° and 51° were performed after the others, and the same incident intensities could not be obtained. This is reflected in the 10-hour yields. The ratio C<sub>2</sub>H<sub>6</sub>/CO decreases with rise of temperature, and it is apparent that at 60° no diacetyl can be formed.

#### DISCUSSION.

The region of the acetone absorption spectrum with which we are concerned, *i.e.*, between 2200 and 3400 Å., has been studied by several workers (Norrish, Crone, and Saltmarsh, *loc. cit.*; Bowen and Thompson, *Nature*, 1934, **133**, 571; Norrish, *ibid.*, p. 837; Noyes, Duncan, and Manning, *J. Chem. Physics*, 1934, **2**, 717), and its main features seem to be well established. The long-wave end of the spectrum shows banded structure, which fades at about 3000 Å. into apparently continuous absorption extending to 2200 Å., whilst the reality of the banded structure is supported by the occurrence of a green fluorescence caused by wave-lengths down to 2800 Å. (Norrish, *loc. cit.*; Fisk and Noyes, *J. Chem. Physics*, 1934, **2**, 654). It is probable that the two types of absorption are superimposed over a considerable range, since, according to Howe and Noyes (*J. Amer. Chem. Soc.*, 1936, **58**, 1404), fluorescence can be observed upon excitation by all mercury lines between 3130 and 2536 Å.

The quantum yield of the decomposition of acetone at 60° is 0.2 for 3130 Å., and 0.4 for 2536 Å. (Damon and Daniels; Norrish *et al.*; *loc. cit.*), whereas Leermakers (*J. Amer. Chem. Soc.*, 1934, **56**, 1899) finds that, in the banded region, the quantum yield approaches unity as the temperature is increased to 160° and then remains constant. Norrish (*Trans. Faraday Soc.*, 1934, **30**, 103) has suggested that with simple ketones the primary photochemical process is a dissociation into radicals, and there are now a considerable number of facts with which this theory is consistent; *e.g.*, the photo-decomposition of methyl ethyl ketone yields carbon monoxide and a mixture of ethane, propane, and butane (Norrish and Appleyard, *J.*, 1934, 874), and Pearson (*ibid.*, p. 1718; Pearson and Purcell, *J.*, 1935, 1151) has detected methyl radicals in the products of the photolysis of acetone

by their reaction with metallic mirrors. Furthermore, according to Leermakers (*loc. cit.*), the photosensitisation of the chain decomposition of dimethyl ether is to be ascribed to the production of radicals. However, it has not hitherto been possible to decide which of the following reactions constitutes the primary photochemical process :

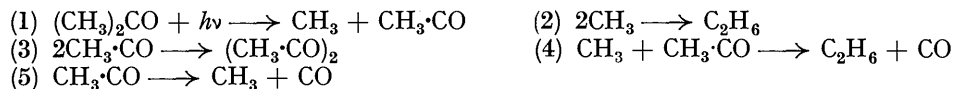


Norrish has stated with reference to this difficulty, that if equation (b) is correct, the acetyl radical must break up spontaneously, since no appreciable quantity of diketone is detectable in the products. Our experiments at 60° are in agreement with this view, but it is evident from the semi-quantitative separation of diacetyl and the value of the  $\text{C}_2\text{H}_6/\text{CO}$  ratio at room temperatures that reaction (b) is the primary process, and that the acetyl radical is capable of a separate existence. Diacetyl had previously been detected in the products of photo-decomposition at room temperatures by Barak and Style (*Nature*, 1935, 135, 307), but in the absence of quantitative data it was not then possible to arrive at definite conclusions as to the nature of the primary process.

The non-gaseous product is mainly diacetyl (see p. 354), and it is probable that the residue consists of polymerides with the same empirical formula. The use of equation (1) for the calculation of the amount of acetone decomposed would therefore appear to be legitimate. Fluctuations of the incident light intensity were unavoidable with our apparatus, but inspection of Table I, *b*, where the data for a number of consecutive experiments with the same arc are given, will show that a 40-fold increase in the intensity is accompanied by a 40-fold increase in the hour yield. The linear relation between light intensity and rate of decomposition is not so obvious in the continuum experiments at constant pressure (Table II), because of the fluctuations of the arc. However, if the percentage of incident light absorbed at the three different pressures shown in Table II is calculated with the aid of the absorption coefficients for acetone (Porter and Iddings, *J. Amer. Chem. Soc.*, 1926, 48, 40), the result is found to be in good agreement with the ratios of the hour yields. The quantum yield is therefore independent of light intensity and of acetone pressure.

Although, in some experiments, the final partial pressure of diacetyl was considerable, no secondary effects due to its presence could be detected. The absorption spectrum of diacetyl covers the same region as that of acetone and extends into the longer wave-lengths as far as the blue, and according to Porter, Ramsperger, and Steel (*ibid.*, 1923, 45, 1827), it is decomposed by ultra-violet light at 100°, yielding 2 vols. of carbon monoxide and 1 vol. of ethane. Norrish, however, has reported (*Trans. Faraday Soc.*, 1931, 27, 405) that the gaseous products contain 85% of carbon monoxide. If either of these processes occurred to a measurable extent in our experiments, the ratio  $\text{C}_2\text{H}_6/\text{CO}$  would be expected to decrease as the period of illumination increased. No such decrease is apparent, and it is to be inferred that at room temperatures diacetyl vapour possesses considerable stability towards light.

*Photo-decomposition in the Continuum Region.*—The ratio  $\text{C}_2\text{H}_6/\text{CO}$  obtained with light of different intensities in the continuum (Table II) for a constant acetone pressure of 160 mm. is plotted against the rate of decomposition of acetone in Fig. 2. The ratio first increases rapidly with increasing intensity, and then approaches a maximum value of about 2·5. If we write down a probable series of intermediate reactions, *viz.*,

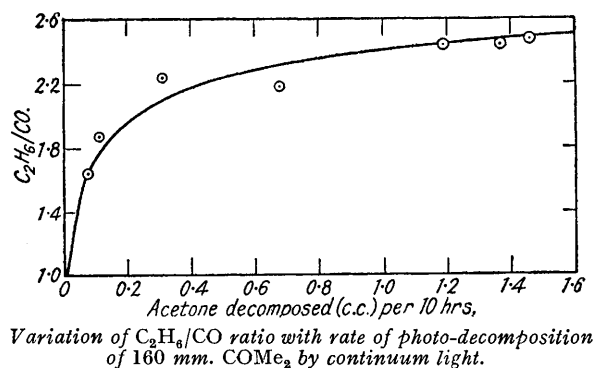


and suppose that at moderate pressures and intensities the stationary concentrations of methyl and acetyl are about the same, the equation  $d[\text{C}_2\text{H}_6]/d[\text{CO}] = 1/(k' + k''/\sqrt{I_{\text{abs.}}})$  can be deduced from the rates of formation and removal of the intermediates. Evaluating the constants with the aid of the experimental results and assuming that  $d[\text{C}_2\text{H}_6]/d[\text{CO}] = \text{C}_2\text{H}_6/\text{CO}$ , we obtain

$$\text{C}_2\text{H}_6/\text{CO} = 1/(0\cdot3391 + 0\cdot077/\sqrt{I_{\text{abs.}}})$$

where  $I_{\text{abs.}}$  represents the hour yield. This relation is plotted in Fig. 2, the experimental points being shown. At very low intensities, the methyl and the acetyl radical concentrations would be widely different, and the above equation, which tends to zero as  $I_{\text{abs.}} \rightarrow 0$ , would no longer apply. The ratio approaches a maximum value at high intensities owing to the operation of reaction (4), which cannot be replaced by the recombination reaction  $\text{CH}_3 + \dot{\text{C}}\text{H}_3\cdot\text{CO} \rightarrow (\text{CH}_3)_2\text{CO}$ . Reaction (5) is necessary to explain the decrease in  $\text{C}_2\text{H}_6/\text{CO}$  at low intensities, and offers the most convenient explanation of the influence of temperature. The relative importance of (5) will increase as the intensity decreases, until ultimately all acetyl radicals will decompose before they can combine by (3) and the ratio will become equal to unity. A secondary generation of acetyl radicals by the reaction  $\text{CH}_3 + (\text{CH}_3)_2\text{CO} \rightarrow \text{C}_2\text{H}_6 + \dot{\text{C}}\text{H}_3\cdot\text{CO}$  is excluded because it introduces the possibility of chains, and it is known that the quantum yield does not become greater than unity at higher temperatures (Leermakers, *loc. cit.*; Norrish and Akeroyd, J., 1936, 190). When the  $\text{C}_2\text{H}_6/\text{CO}$ -hour-yield data for the experiments at 70 mm. and 32 mm. (Table II) are plotted, the points are found to lie considerably below the curve for 160 mm. (Fig. 2), *i.e.*, the ratio decreases with the pressure. This behaviour would be expected if reaction (5) were wholly or partly heterogeneous, since diffusion to the walls would be facilitated by decrease of pressure. Alternatively, if reactions (2) and (3) required the intervention of a third

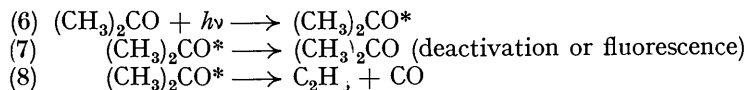
FIG. 2.



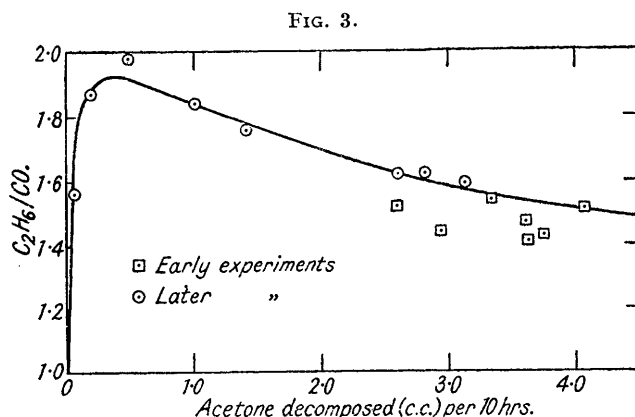
molecule, the ratio would again be less at the lower pressures. It appears to be the total pressure which is concerned here, and not simply the acetone pressure, since the ratio in long experiments with about 50% of decomposition (Table II) is the same as in short experiments in which only a small fraction of the acetone is decomposed. The fall in the light absorption would have only a slight effect on the ratio at high intensities (Fig. 2), but if it depended on the partial pressure of acetone, a considerably smaller value would be expected with a large percentage of decomposition. The products of decomposition as well as acetone itself, therefore, either facilitate reactions (2) and (3) or prevent the diffusion of acetyl radicals to the walls.

*Photo-decomposition in the Banded Region.*—A value for the quantum yield in the banded region at room temperatures is given by Leermakers (*loc. cit.*), *viz.*, 0.04, and the very slow rate of decomposition obtained in our experiments (Table III) can only be accounted for if the quantum yield is very much smaller than in the continuum. Moreover, if the values of  $\text{C}_2\text{H}_6/\text{CO}$  are plotted against the hour yield, the points will be found to lie well below the continuum curve (Fig. 2). In other words, the low value of the ratio cannot be ascribed to the smallness of the hour yield. Since all radiation below 3130 Å. is cut off by the Pyrex plate, and all below 2950 Å. by the chromate filter, there would appear to be a photochemical threshold at about 3000 Å., on the short-wave side of which the type of decomposition described in Table II occurs, and on the long-wave side of which we have another type in which the ratio  $\text{C}_2\text{H}_6/\text{CO}$  is unity. However, a sharply defined threshold is scarcely to be expected because of the overlapping of the banded and continuous absorption to which allusion has already been made. Absorption in the continuum leads

to the production of free radicals, and in these circumstances the ratio  $C_2H_6/CO$  must depend on the conditions. On the other hand, if we suppose that light absorption in the banded region yields an excited molecule which is deactivated either by collision or by fluorescence, or which produces ethane and carbon monoxide directly, the experimental result that  $C_2H_6/CO = 1$  can be explained. Patat (*Z. physikal. Chem.*, 1934, B, 25, 208; Patat and Löcker, *ibid.*, 1935, B, 27, 431) has suggested that a similar state of affairs exists in the case of formaldehyde. The suggested mechanism for the photo-decomposition in the banded region is therefore :



Norrish has supposed that the primary dissociation into radicals in the continuum necessitates a radiationless transition from an upper excited state to a second unstable state. Essentially the same process is envisaged for the band region, with the exception that the unstable state is different and leads to normal molecules instead of radicals. The fact that Leermakers's experiments in the banded region at higher temperatures appear to



Variation of  $C_2H_6/CO$  ratio with rate of photo-decomposition of 160 mm.  $COMe_2$  in the full arc.

involve radical decomposition does not invalidate the above mechanism. It is possible that, when light in the banded region is absorbed by molecules in high vibrational levels, the probability of transition from the excited state to an unstable state yielding radicals is increased to such an extent that the decomposition into normal molecules becomes negligible. This is rendered probable by that fact that light of wave-length 3130 Å. possesses just sufficient energy to effect the decomposition into radicals.

*Photo-decomposition in the Full Arc.*—The experimental data for different intensities of the full arc (Table I, a and b) are plotted in Fig. 3. Consideration of the hour yields given in Tables II and III shows that by far the greater part of the decomposition occurring in the full arc is due to the continuum light. The published transmission values of the filters for the band region being used, the maximum diminution in the ratio which can be ascribed to the presence of light in the banded region is 0.2. For higher intensities, the ratio is about 2.5 in the continuum and 1.5 in the full arc. The decomposition occurring in the banded region alone is therefore much too small to account for the difference. However, it is possible that excited acetone molecules produced in this region are particularly efficient in effecting the decomposition of acetyl radicals on collision. Moreover, the fact that fluorescence occurs in acetone at relatively high pressures is evidence of the comparative stability of the excited state. On the basis of a scheme consisting of reactions (1)—(8), together with reaction (9),



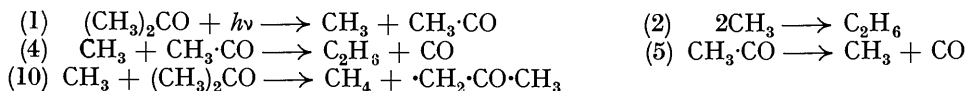


and on the same assumption as before relative to the stationary concentrations of methyl and acetyl, the expression  $d[\text{C}_2\text{H}_6]/d[\text{CO}] = (1 + k'\sqrt{I})/(k'' + k'''\sqrt{I} + k''''/\sqrt{I})$  can be derived. It has also been assumed that the quanta absorbed in the banded region and in the continuum are proportional to one another. This will be correct so long as the acetone pressure remains constant. Giving suitable numerical values to the constants, we obtain

$$\text{C}_2\text{H}_6/(\text{CO}) = (1 + 0.001\sqrt{I})/(0.35 + 0.145\sqrt{I} + 0.05/\sqrt{I}).$$

The curve plotted in Fig. 3 represents this relation. Although the early data from Table I, *a* lie somewhat below the line at high intensities, later experiments with a more refined technique (Table I, *b*) gave results in close agreement with the theory. Reaction (9), which represents the supposed interaction of the products of absorption in the banded region with those of the continuum, is therefore responsible for the decrease in the ratio at higher intensities.

*The Influence of Temperature.*—Careful repetition of Norrish, Crone, and Saltmarsh's experiments at 60° failed to confirm their claim that with pure acetone and with filtered light of low intensity, the sole products are carbon monoxide and ethane in equal volume. For similar rates of decomposition, we found 27.8% of methane in the gaseous products and a  $\text{C}_2\text{H}_6/\text{CO}$  ratio of 0.37. On the other hand, our analytical data for the full arc (Table IV) are in agreement with the results of their refluxing experiments (*loc. cit.*), which gave CO, 46.6;  $\text{CH}_4$ , 9.2;  $\text{C}_2\text{H}_6$ , 44.2%. Methane is therefore one of the major products of reaction under these conditions and its appearance is not due to the presence of liquid acetone, as Norrish has suggested. When a series of experiments with about 70 mm. of acetone at different temperatures are compared, the  $\text{C}_2\text{H}_6/\text{CO}$  ratio is found to approach unity with rise of temperature (Table V). Very little methane was formed at this pressure. The proportion of methane in the products at 60° increases therefore (*a*) with the acetone pressure and (*b*) when the light intensity is diminished (Table IV). This behaviour can be accounted for by a scheme first proposed to explain the thermal decomposition of acetone (Rice and Herzfeld, *J. Amer. Chem. Soc.*, 1934, 56, 284; Rice, Rodowskas, and Lewis, *ibid.*, p. 2457) and applied later to the photo-decomposition at high temperatures (Leermakers, *loc. cit.*; Patat, *Z. physikal. Chem.*, 1935, B, 31, 105), *viz.*,



The radical  $\cdot\text{CH}_2\cdot\text{CO}\cdot\text{CH}_3$  combines either with itself to form acetylacetone or with a methyl radical, giving methyl ethyl ketone. The only difference between this and the low-temperature scheme for the continuum lies in the inclusion of reaction (10). The reaction yielding diacetyl is omitted as this obviously is not formed. According to Leermakers, reaction (10) occurs readily at 400° but not at 200°, since the products not condensed by liquid air contain 33.3% of carbon monoxide at 400° and 50% at 200°. The remaining 66.6% at 400° was assumed to be methane, yet although gas analyses were not carried out, the remaining 50% at 200° was taken to be ethane. We have found, however, that ethane can be quantitatively removed by liquid air, and there seems to be little doubt that at 200° the residual gas was methane and not ethane as previously supposed. These results indicate therefore, that reaction (10) occurs readily at 200°, and our experiments show that it already begins to be of importance at 60°. With 80 mm. pressure of acetone, methyl groups disappear by other reactions, but as the pressure is increased to 840 mm., collisions with acetone become more frequent, until 20% of methane is produced by reaction (10). Furthermore, when the light intensity is decreased, methyl radicals suffer fewer collisions with one another and with acetyl, with the result that reaction (10) becomes of greater importance, in agreement with the observed increase in the percentage of methane.

Our previous conclusions with regard to the stability of the acetyl radical (*Nature*, 1936, 138, 206) are fully confirmed by the results given in Table V. As the temperature is reduced, the ratio  $\text{C}_2\text{H}_6/\text{CO}$  and the amount of diacetyl formed steadily increase, and

the reaction tends to take the course  $(\text{CH}_3)_2\text{CO} + h\nu \longrightarrow \text{CH}_3 + \text{CH}_3\cdot\text{CO} \longrightarrow 0.5\text{C}_2\text{H}_6 + 0.5(\text{CH}_3\cdot\text{CO})_2$ . The acetyl radicals are therefore comparatively stable at  $0^\circ$ , but at  $60^\circ$  all are decomposed by collisions in the gas phase (cf. high-pressure experiments, Table IV) or at the wall of the vessel (cf. p. 358 and Table V). Glazebrook and Pearson (private communication) have made a direct investigation of the acetyl radical by the mirror method and have arrived at similar conclusions.

There can now be no doubt that, from the chemical point of view, the photo-decomposition of acetone is not an essentially simple process accompanied by relatively unimportant side reactions, but that any one of several more or less complicated courses is possible under each set of conditions. It is proposed to extend the investigation by a detailed study of the quantum yield.

## SUMMARY.

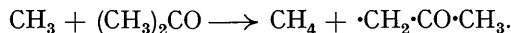
The absorption of light by acetone in the region of continuous absorption yields methane, ethane, carbon monoxide, and diacetyl, as a result of the primary process,  $(\text{CH}_3)_2\text{CO} + h\nu \longrightarrow \text{CH}_3 + \text{CH}_3\cdot\text{CO}$ .

The ratio  $\text{C}_2\text{H}_6/\text{CO}$  increases with increasing intensity of continuum light to a maximum value of about 2.5, and an equation has been deduced from a probable mechanism which accounts for this behaviour.

It is suggested that light absorption in the banded region leads to the production of an excited molecule which may dissociate directly into ethane and carbon monoxide without the intervention of radicals.

With the full light of the mercury arc at  $20^\circ$ , the ratio  $\text{C}_2\text{H}_6/\text{CO}$  increases to a maximum value of about 1.9, and then decreases to 1.5 as the light intensity is increased. This can be explained if it is supposed that the excited molecules produced in the band region interact with acetyl radicals arising from the absorption of light in the continuum.

The effective life of the acetyl radical rapidly decreases as the temperature is raised. Increase of acetone pressure or decrease of light intensity increases the proportion of methane in the products at  $60^\circ$ , owing to the operation of the reaction



We thank the Chemical Society for a grant towards the cost of apparatus.

THE UNIVERSITY, LEEDS.

[Received, January 11th, 1937.]