# 318. *Primary Photochemical Reactions. Part V. The Spectroscopy and Photochemical Decomposition of Acetone.*

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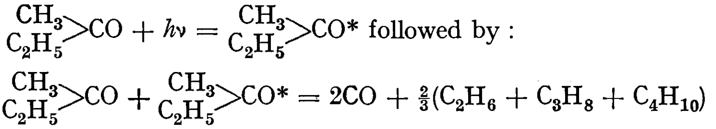
The photochemical decomposition of ketones is known to occur when the dry vapour is irradiated with light corresponding to the absorption band of the carbonyl group (*ca.* λλ 3200—2200 Å.). Simple unsymmetrical ketones yield a mixture of hydrocarbons and carbon monoxide: *e.g.*, methyl ethyl ketone decomposes approximately according to the equation (Part IV; Norrish and Appleyard, this vol., p. 874) $CH_3{\cdot}CO{\cdot}C_2H_5 \longrightarrow CO + \frac{1}{3}(C_2H_6 + C_3H_8 + C_4H_{10})$. For acetone, Damon and Daniels (*J. Amer. Chem. Soc.*, 1933, **55**, 2363) find quantum efficiencies of 0·2, increasing to 0·4 between λλ 3130 and 2650 Å. This has been confirmed in the present paper. These simple results may be explained by either of the following mechanisms:

(1)



$$\begin{matrix}CH_3\\C_2H_5\end{matrix}\!>\!CO + h\nu = \begin{matrix}CH_3\\C_2H_5\end{matrix}\!>\!CO^* \text{ followed by :}$$

$$\begin{matrix}CH_3\\C_2H_5\end{matrix}\!>\!CO + \begin{matrix}CH_3\\C_2H_5\end{matrix}\!>\!CO^* = 2CO + \tfrac{2}{3}(C_2H_6 + C_3H_8 + C_4H_{10})$$

or (2)

$$CH_3{\cdot}CO{\cdot}C_2H_5 + h\nu = CO + CH_3 + C_2H_5 \text{ followed by :}$$
$$CH_3 + C_2H_5 = \tfrac{1}{3}(C_2H_6 + C_3H_8 + C_4H_{10})$$

*i.e.*, either by the postulation of molecular activation, or by assuming the primary production of free radicals which combine to give a mixture of hydrocarbons.

The former explanation has been suggested by Damon and Daniels (*loc. cit.*) and accepted by Noyes (*Rev. Mod. Physics*, 1933, **5**, 280). The latter, first suggested by one of us (Norrish, *Trans. Faraday Soc.*, 1934, **30**, 103), represents our view.

To explain the low quantum efficiency, Damon and Daniels assume that some collisions of excited molecules are unreactive and lead to the degradation of the energy of excitation to heat. We have concluded, on the other hand, that the primary dissociation process itself is inefficient, and that a proportion of molecules which absorb quanta are not dissociated, their energy being degraded to heat by an internal process.

It is not possible to choose between these two mechanisms without further experimental data. If the first theory is correct, we should expect the ketone to have an absorption spectrum showing discrete structure of vibration and rotation; for the upper level is regarded as stable and unreactive except on collision. For the same reason, it should also show fluorescence at reduced pressures. So far as was known at the time of their work, acetone did show fluorescence, but the spectrum was believed to be continuous. Spectroscopic indications were therefore conflicting, for a true continuous spectrum is a sure indication of molecular dissociation. In the present paper we have therefore studied the problem from this point of view, and have made a careful examination of the absorption and fluorescence of acetone, as well as of its photochemical decomposition. From all our results we have concluded that the mechanism involving primary dissociation into radicals is the correct one. This raises an issue of fundamental importance to the problem of the decomposition of polyatomic molecules in general, *viz.*, the mechanism by which those molecules which give a diffuse spectrum and no fluorescence lose their energy without dissociating. We discuss this matter on p. 1463.

## EXPERIMENTAL.

*Preparation of Acetone.*—The whole of the acetone used in this work was purified by the method of Shipsey and Werner (J., 1913, **103**, 1255). The acetone was distilled from its sodium iodide compound on a steam-bath, dried for 24 hours over calcium chloride, and distilled, first and last fractions being rejected. The whole process was then repeated; at the final distillation the b. p. was constant to 0·1°, and within 0·3° of the b. p. for the existing atmospheric pressure given in the international critical tables.

*The Ultra-violet Absorption Band of Acetone.*—Acetone, in common with all ketones and aldehydes, has an absorption region in the near ultra-violet lying between 3300 and 2200 Å., and characteristic of the carbonyl group. This band has frequently been observed and described as continuous, showing a maximum at 2800 Å. Damon and Daniels (*loc. cit.*) agreed with other workers in describing it as structureless. This statement, however, was at variance with the observation of fluorescence, since this can only be produced by absorption in a region of discrete structure, and it seemed probable that part at least of the acetone absorption band should show fine structure. This has been fully verified by our photographs. Using a column of

1 m., and vapour pressures from 0·2 mm. to 140 mm., a region of discrete structure on the long-wave side of the continuous absorption band has been observed. The spectrum was photographed by means of a Rowland's concave grating of 3 m. focal length, and giving a dispersion of 5·3 Å. per mm. in the first order. The source of ultra-violet radiation was a water-cooled hydrogen lamp of the Bay and Steiner type, yielding a continuous emission from 3800 to 2000 Å. The absorption tube was of quartz, 1 m. long, with plane end plates fused on; it was connected by a ground joint to a reservoir of pure acetone and to a Hyvac pump. The vapour pressure of acetone could be controlled by freezing-mixtures of solid carbon dioxide–ether, ice–hydrochloric acid, ice, etc.

The absorption spectrum obtained consisted of two parts partially overlapping. First came a discontinuous region extending from 3326 to 2945 Å.; then from 2945 to 2200 Å., where it died out, the absorption was continuous and structureless. The transition did not appear completely sharp, the former region appearing to overlie the latter for a short distance of about 200 Å., between 3100 and 2900 Å. This overlap was greatest at the higher pressures. One of our photographs is reproduced in Fig. 1. The discrete part of the spectrum is very complicated and crowded, and may consist of the unresolved rotational structure of a single complex band, or alternatively of a set of bands, fairly close together and completely overlapping each other. A photograph of this region using the second order of a 6 m. grating would probably be worthy of study. For our present purpose, it is sufficient to have resolved the absorption band into this region of discrete structure.

In order to confirm the continuous structure of the absorption band beyond about 3000 Å., further photographs were taken on a Hilger small quartz and a Hilger E 1 (dispersion 6·7 Å/mm. at 3300, and 2·6 Å./mm. at 2500) spectrograph. Tubes 1 m. and 5 m. long were employed, and the pressure of acetone varied from 0·1 to 160 mm. These photographs completely verified those obtained with the grating. With the exception of the region of discrete structure between 3300 and 3000 Å. described above, the absorption spectrum was quite continuous.

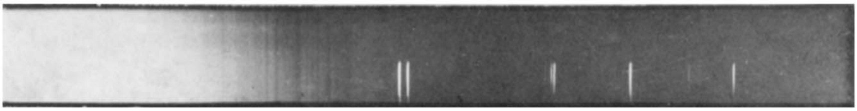
Snow and Eastwood (*Nature*, 1934, **133**, 908), on photographing the spectrum of acetone with low dispersion, found three or four faint maxima of absorption in the continuous spectrum. These we have confirmed; they are separated by about 1100 wave-numbers, in agreement with a characteristic Raman frequency of the carbonyl group.

*The Fluorescence of Acetone Vapour.*—The fluorescence was observed in a quartz tube, 5 cm. long and 4 cm. in diameter, with quartz end plates fused on, and with a side limb attached to act as a reservoir for the acetone. The whole apparatus was first evacuated by means of a mercury-diffusion pump. Pure acetone was then distilled into the reservoir, which was kept cool in liquid air. The observation chamber and reservoir were then sealed off from the distillation and pumping system. The pressure of acetone in the tube was controlled by various freezing mixtures.

The fluorescence was excited by light from a horizontal mercury arc, which was focused from outside the dark room by means of a large-aperture quartz lens fixed in a hole in the wall. The light was filtered through a plate of Chance's glass, so that only light of wave-length λλ 3800—3300 Å. entered the room, and the fluorescence could be examined in darkness. When the sharply focused beam of ultra-violet light was allowed to fall into the cell, its path was shown up by a brilliant band of greenish fluorescence, the intensity of which diminished with diminution of the pressure of acetone, and disappeared when the side arm was cooled in liquid air. In agreement with the work of Damon and Daniels, it was found that the addition of a few mm. of oxygen to the acetone reduced the intensity and changed the colour of the emitted light from greenish to bluish. After a period of illumination, the original fluorescence reappeared. Addition of nitrogen, however, had no effect on the character of the fluorescence. These results are explained if we assume that, while unaffected by inert gases, the fluorescence is specifically quenched by the chemical action of oxygen with the excited molecules of acetone. In course of time, the oxygen is removed by this reaction and the original fluorescence reappears. The transient fluorescence must be ascribed to some intermediate product.

The fluorescence was photographed and examined visually in a constant-deviation flint-glass spectroscope giving a dispersion of 93 Å./mm. at $\lambda = 5000$ Å. and 200 Å./mm. at $\lambda = 6100$ Å. The mercury and the neon spectra were used for comparison. Both visually and photographically, it was found to consist of three diffuse bands devoid of structure. The frequency separation of these bands was 1500—1600 wave-numbers and is of the same order as the Raman frequency characteristic for the carbonyl group (1700). Measurements are given below.

Fig. 1.



| | Wave-length, Å. | Int. | Wave-no., in vac. | δν. |
|---|---|---|---|---|
| Edge of band | 5034 | | | |
| Maximum | 5117 | 10 | 19,540 | |
| Edge of band | 5244 | | | 1600 |
| Edge of band | 5458 | | | |
| Maximum | 5572 | 3 | 17,940 | |
| Edge of band | 5699 | | | 1530 |
| Edge of band | 5917 | | | |
| Maximum | 6095 | 2 | 16,410 | |
| Edge of band | 6303 | | | |

The discrete fluorescence in the ultra-violet region referred to in a preliminary account of this work (*Nature*, 1933, **132**, 241) has not been confirmed. Unfortunately, a number of weak lines from the anode of the mercury lamp in the region 3300—3800 Å. were transmitted by the colour filter and scattered into the spectrograph. Owing to difficulty with this scattering, we have not yet been able to make certain whether the fluorescent emission of acetone extends down to the exciting line or not.

*The Infra-red Absorption of Acetone.*—By comparison of the magnitudes of the absorbed and the emitted quanta, it may be inferred that the fluorescence of acetone is associated with levels corresponding to absorption in the infra-red and lying between 7100 and 10,000 Å. (Fig. 2). The existence of such an absorption region in acetone had not hitherto been suspected. We have, however, detected it by photographic means, using a small-grating spectroscope giving a dispersion of 41 Å./mm., in the first order, and either a carbon arc or Pointolite lamp as source. Eastman mesocyanin (Type III P) and xenocyanin (Type III Q) plates, both sensitised in dilute ammonia and developed to maximum contrast with metol–hydroquinone developer, were employed. First-order iron-arc standards were photographed on the plates before and after exposure.

FIG. 2.

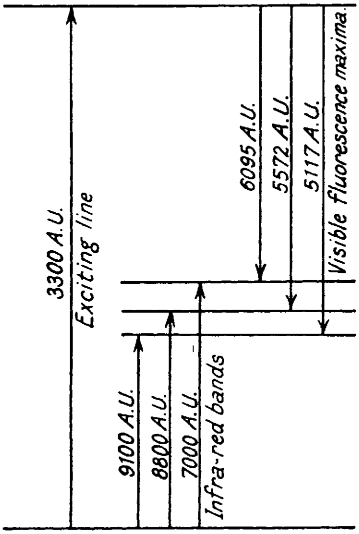
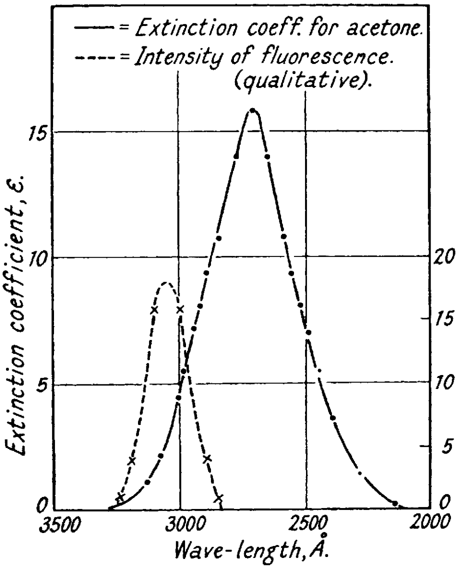


FIG. 3.



With a column of vapour 1 m. long, no absorption was observable, but with a column of pure liquid acetone 0·6 m. long, a set of absorption bands, all diffuse and of varying intensities, was obtained. The wave-lengths were measured, and are recorded below.

*New Infra-red Absorption of Acetone.*

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| Wave-length, Å. | 7,205 (1) | 7,346 (2) | 7,488 (2) | 8,737 (1) | 8,851 (10), 9,166 | 9,807 (2) | 9,987 (10) |
| Wave-number, in vac. | 13,879 | 13,613 | 13,355 | 11,450 | 11,300 | 10,190 | 10,010 |

This infra-red absorption of acetone is far removed from the absorption lying between **3·42** μ and **13·1** μ measured by Coblenz (" Investigations of Infra-red Spectra," Carnegie

Institution, No. 905, p. 200). It is in precisely the position indicated by the fluorescence measurements recorded above.

*The Relation between the Fluorescence and the Ultra-violet Absorption Band.*—It is to be expected that fluorescence will only be produced by absorption in that part of the spectrum showing discrete structure. In order to test this point, use was made of a large-aperture quartz monochromator, and a powerful hydrogen lamp consuming 2 amps. at 4000 volts, kindly put at our disposal by Dr. Schulman of the Department of Colloid Science. The lamp gave a continuous spectrum of nearly uniform intensity over a wide range. Used in conjunction with the monochromator, it afforded beams of ultra-violet radiation, approximately monochromatic in character, the wave-length range in any given beam being regulated by the slit of the instrument. Since these beams were of approximately the same intensity, they could be used to compare the variation of the fluorescence of acetone with the wave-length of the stimulating light. The same observation cell as was used in the photography of the fluorescence was employed. It was interposed in the path of the beam, and the fluorescence observed at right angles to the beam through the plane end plates. The following observations were made :

| Wave-length of exciting radiation, Å. | Character of fluorescence. | Wave-length of exciting radiation, Å. | Character of fluorescence. |
|---|---|---|---|
| 2500—2600 | None | 2900—3100 | Strong |
| 2650—2750 | None | 3000—3200 | Strong |
| 2700—2900 | Just visible | 3100—3300 | Moderate |
| 2800—3000 | Moderate | 3150—3400 | Faint |

These results are plotted in Fig. 3 in comparison with the ultra-violet absorption of acetone vapour as measured spectrophotometrically by Porter and Iddings (*J. Amer. Chem. Soc.*, 1926, **48**, 40). For this purpose an arbitrary scale of intensity of fluorescence based on our visual observations was employed, *viz.*, faint = 1, moderate = 4, strong = 16. It will be seen that the fluorescence is stimulated by the absorption of light exactly corresponding in wave-length to the region of sharp discrete structure observed in the absorption spectrum.

The maximum intensity of fluorescence is stimulated by light of wave-length 3050 Å.; on the other hand, that of absorption is at 2700 Å in the region of continuous absorption which produces no fluorescence at all. The correlation between the discrete character of the absorption and the incidence of fluorescence is thus complete.

*The Photochemical Decomposition of Acetone.*—There are two points of major importance to be decided in this chemical aspect of the problem : (1) The nature and proportions of the products of decomposition, the latter determination being necessary in order to find which is the main reaction and which secondary. (2) The relative effects of various wave-lengths in the decomposition of acetone vapour, and especially a comparison of those falling within the discrete and the continuous part of the ultra-violet absorption spectrum. This may be achieved by the measurement of the quantum efficiency of decomposition in monochromatic light.

*The products of photodecomposition of acetone, and the nature of the primary reaction.* Purified acetone was refluxed in a vacuum in a quartz flask under illumination from a quartz–mercury lamp. The apparatus has been fully described (Part IV, *loc. cit.*). After the illumination had continued for some 30 hours, the products of decomposition were pumped off by the Toepler pump, and collected in three fractions. The first fraction was pumped off through a liquid-air trap, the quartz flask being similarly cooled; it contained mainly carbon monoxide, but also some methane; it would have contained any hydrogen if present. The second fraction was pumped off through a liquid-nitrogen–pentane bath at − 145° to − 150°, and would contain any ethylene, together with small quantities of ethane, which has a small vapour pressure at this temperature. The third fraction was pumped off at − 110°, using a cooling bath of alcohol and liquid air, and would contain ethane, higher hydrocarbons, and carbon dioxide. The analysis of the three fractions was as follows : (i) (25·4 c.c. at *N.T.P.*) 21·2 c.c. carbon monoxide (by absorption in ammoniacal cuprous chloride), 4·2 c.c. methane (by explosion), no oxygen; (ii) (3·5 c.c. at *N.T.P.*) all ethane (by explosion), no unsaturated hydrocarbons or carbon dioxide; (iii) (16·4 c.c. at *N.T.P.*) all ethane, no carbon dioxide or unsaturated hydrocarbons.

From these results, the following composition may be calculated for the gaseous products of decomposition : CO, 46·6; $CH_4$, 9·2; $C_2H_6$, 44·2%. Damon and Daniels, however, obtained the following : CO, 47; $CH_4$, 13·2; $C_2H_6$, 27·9; $H_2$, 4·2; $CO_2$, 3·6%. With this result we are unable to agree, for the following reasons :

(1) We have carried out many decompositions of ketones homologous with acetone by the method described above, and have never obtained either carbon dioxide or hydrogen among the

products, *except* in cases where the ketone could be shown to contain a carboxylic acid as an impurity, or when air was allowed to leak into the apparatus. With acetone itself in the presence of air, carbon dioxide was readily obtained. Berthelot and Gaudechon (*Compt. rend.*, 1910, **151**, 478; 1912, **155**, 207) similarly reported only the formation of carbon monoxide, ethane, and methane from acetone, and would have surely detected carbon dioxide and hydrogen had they been formed.

(2) The percentages of ethane and methane recorded by Damon and Daniels were obtained by indirect combustion of the mixture, a method which cannot give results comparable in accuracy with the fractionation method used above.

We believe that the source of the hydrogen and carbon dioxide recorded by Damon and Daniels is either the secondary decomposition of some intermediate compound formed as a side issue in the direct illumination of the liquid acetone, or the chance entry of air into their apparatus.

It will be seen that the carbon monoxide and ethane in our analysis are nearly equivalent to each other. It is clear, however, that small quantities of less volatile substances accumulate in the acetone during prolonged irradiation, for the liquid turns slightly yellow. If the liquid be screened as far as possible from the light, however, this effect is reduced to a minimum and would appear to be the result of photochemical reaction induced in the liquid itself. It seems probable that the methane results from the decomposition of some compound produced in this way, for, when using filtered light and weaker intensities in the measurements of quantum yield described in the next section, we were unable to obtain any methane, and found that carbon monoxide and ethane constituted the whole of the reaction products.

In view of the equivalence of the ethane and carbon monoxide and of the above considerations, we conclude that decomposition in the gas phase is practically quantitative according to the stoicheiometric equation $CH_3{\cdot}CO{\cdot}CH_3 = C_2H_6 + CO$. It therefore becomes pertinent to inquire whether the ethane molecule has its origin in a single molecule of acetone or whether some other mechanism is operative. Since, however, the analogous decomposition of methyl ethyl ketone (Part IV, *loc. cit.*) affords a mixture of ethane, propane, and butane, the change cannot take place in this simple way; but the analytical results are suitably explained if the reaction follows one of the two courses indicated on p. 1457, which are criticised later.

*The quantum yield of the photodecomposition of acetone.* Damon and Daniels (*loc. cit.*), using a mercury lamp and a monochromator, found $\gamma = 0{\cdot}2$—$0{\cdot}3$ at 3130 Å. and 0·3—0·4 at 2650 Å. It will be observed that while the first wave-length falls within the region of the spectrum showing discrete structure and fluorescence, the second corresponds to the apparent continuum where fluorescence is absent. In this region, our previous experience with nitrogen peroxide would have led us to expect a value of unity, and it seemed worth while to repeat the measurements by a different method to check this interesting anomaly, but we too found low values.

The decomposition was carried out at constant vapour pressure of acetone at 60° in identical sealed quartz bulbs of 200 c.c. capacity; each bulb had a short stem of quill tubing about 5 cm. in length, and a second tube through which it could be filled and sealed off at a constriction.

After they had been thoroughly baked out under high vacuum, about 1 c.c. of pure acetone was distilled into the stem of each bulb by the use of liquid air, and the bulb was sealed from the distillation apparatus. Two of these bulbs were mounted side by side in an oven, carefully regulated to 60°, with their stems vertically downward. Through suitable quartz windows, two beams of light from a horizontal mercury-vapour lamp traversed the oven, and passed diametrically through the bulbs. One beam was of wave-length 3130 Å. the other of 2750—2480 Å.; they were focused alternately by identical optical systems on to a sodium photoelectric cell, which had been calibrated for each wave-length against a thermopile previously standardised against an N.P.L. standard lamp.

The mercury lamp was of the horizontal type, and was run from a battery of cells at a constant voltage of 135 and a current of 3·0 amps. Irradiation was maintained for 15 or more hours, the incident and transmitted radiation being determined from time to time and found to remain constant. At the end of this period, the bulbs were inverted, and opened over mercury by nipping the end of the constriction. The mercury entered and compressed the gaseous products into the closed stem where their volume was measured under atmospheric pressure, allowance being made for the vapour pressure of acetone. The gas was then introduced into a microgas burette and analysed for carbon monoxide. This was found to be always about 50%. The residual gas exploded as pure ethane; a small quantity of ethane dissolved in the acetone. No evidence of methane or carbon dioxide was found, and it seems probable that with monochromatic light of low intensity in the absence of any liquid, the decomposition occurs quantitatively to carbon monoxide and ethane. The quantum efficiency was then calculated from the carbon monoxide produced and the number of quanta absorbed, as described by Norrish and Kirkbride (J., 1932, 1518). Corrections for light losses by reflexion were determined directly, and amounted to about 20%.

Similar experiments were carried out with light of wave-length 3650 Å., and also a blank experiment to prove the absence of any thermal decomposition.

Colour filters as described by Bowen (J., 1932, 2236) were used to isolate the various wave-lengths. They were contained in quartz cells of 5 cm. diameter with plane end-plates fused on. These filters transmitted varying amounts of visible light in addition to their specific ultra-violet regions. Since, however, the photoelectric cell was nearly insensitive to these visible wave-lengths, only a small correction was needed. This was determined directly as previously described by Norrish and Kirkbride (*loc. cit.*).

The following results were obtained :

(1) *Calibration of photoelectric cell–galvanometer system, giving erg sensitivity and quantum sensitivity per cm. deflexion of the galvanometer.*

| P.D. on cell, volts | 93 | | 112 | 215 | |
|---|---|---|---|---|---|
| Wave-length, Å. | 2480—2770 | 3130 | 3650 | 2480—2770 | 3130 |
| Ergs/sec. | 1660 | 650 | 591 | 655 | 256 |
| Quanta/sec. × $10^{-14}$ | 2·25 | 1·04 | 1·10 | 0·885 | 0·41 |

(2) *Measurement of quantum yield.*

Temp. 60°; pressure of acetone, 860 mm. Hg.

| λ. | 2480—2770. | | 3130. | | 3650. | (Dark.) |
|---|---|---|---|---|---|---|
| | (1). | (2). | (1). | (2). | | |
| P.D. on cell, volts | 93 | 215 | 93 | 215 | 112 | — |
| Incident intensity, cm. defln. | 12·25 | 8·55 | 22·6 | 35·6 | 18·5 | — |
| Transmitted do., cm. defln. | 2·32 | 1·76 | 3·12 | 4·8 | 17·8 | — |
| Time of irradiation, hrs. | 15 | 15 | 15 | 15 | 76 | 15 |
| Quanta absorbed × $10^{-19}$ | 4·75 | 3·25 | 4·3 | 6·82 | 0·2 | — |
| Vol. CO formed, c.c. at N.T.P. | 0·73 | 0·57 | 0·38 | 0·47 | 0·0 | 0·0 |
| Mols. decomp. × $10^{-19}$ | 1·98 | 1·5 | 1·04 | 1·27 | 0·0 | 0·0 |
| Quantum yield | 0·42 | 0·46 | 0·24 | 0·19 | 0·0 | — |

Our results are in good agreement with those recorded by Damon and Daniels, and it is thus established : (1) that acetone is decomposed photochemically within the region of fluorescence and fine structure with a quantum yield of 0·2; (2) that the quantum yield in the diffuse part of the spectrum where fluorescence is absent is greater than that in the region of discrete structure but considerably less than unity.

## DISCUSSION OF RESULTS.

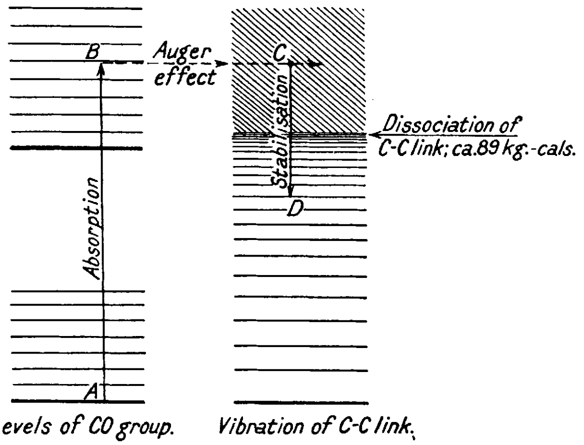
From the varied spectroscopic and chemical results just described, it is possible to construct a tolerably complete picture of the photochemistry of acetone vapour. In the first place, one can now distinguish between the two hypotheses of activation and dissociation referred to on p. 1457. The absence of any structure in that part of the absorption spectrum lying between 2900 and 2200 Å. is in agreement with the inability to excite fluorescence in this region, and confirms the view that the primary photochemical effect is a molecular disruption. Such a disruption must give free hydrocarbon radicals for reasons which have already been made clear (Part IV, *loc. cit.*). In the region of the absorption spectrum between 3300 and 3000 Å. there is discrete structure and fluorescence is readily excited; in this region, therefore, we have excited molecules which do not decompose but lose some of their energy as fluorescence. It is unlikely, however, that any of these excited molecules of acetone react with other molecules of acetone, as suggested by Damon and Daniels (*loc. cit.*), for the fluorescence is not diminished but increased as the pressure of acetone is increased, at least as far as 180 mm., the limit of our observations. The fact that the fluorescence is also visible in liquid acetone lends further support to this view.

Photochemical reaction, however, occurs in the region of discrete as well as in that of continuous absorption, but with diminished efficiency. It is evident that at about 3000 Å. there exists a threshold, signalised by the cessation of fluorescence, and the loss of discrete structure in the spectrum, and it is significant that the energy of the quantum at this point (94,500 cals.) corresponds approximately to the energy of the C–C link.

The probability of molecular decomposition increases as we pass through the threshold, but even in the region of continuous absorption, where there is no fluorescence, it is not unity; *e.g.*, at 2650 Å. only 40% of the molecules which absorb light actually decompose. We are thus presented with a problem fundamental to the photochemistry and spectroscopy of polyatomic molecules, *viz.*, the fate of those molecules which absorb light in a continuous region of the spectrum, but neither fluoresce nor decompose.

The answer to this question involves a perfectly logical extension of our ideas of predissociation. When two atoms of a simple gas such as sulphur come together, they are unable to combine unless a third body is present to remove the energy of recombination. Conversely, if a molecule of sulphur absorbs a quantum of light greater than 100 kg.-cals. it will dissociate by the familar process of predissociation, unless the energy is removed by a collision within the space of $10^{-13}$ sec. The chance of this happening is virtually nil at atmospheric pressure. Thus, inside the region of diffuse absorption, where there is no fluorescence, every molecule of sulphur which absorbs a quantum must dissociate, and the quantum efficiency is unity. If we translate these ideas to the recombination of free radicals and the predissociation of polyatomic molecules, however, the situation is modified by the fact that the polyatomic molecule has many internal degrees of (vibrational and rotational) freedom which can exert a stabilising effect similar to that of a third body in collision. Thus if a methyl radical and an acetyl group come into collision, it does not follow that a third body is required to stabilise their combination. The excess energy may be taken up by the other vibrational and rotational degrees of freedom of the molecule, and the larger the molecule, the greater is the probability that this will occur. Similarly, in the reverse process, the predissociation of such a molecule, it does not follow that rupture will always occur when an energy quantum of the right magnitude is absorbed in the region of continuous absorption. This will only occur if the internal condition of the molecule is favourable. Otherwise the molecule will be stabilised by the loss of some of the energy to other degrees of freedom. A diagrammatic representation of this is shown in Fig. 4. The quantum of light is absorbed by the carbonyl group along *AB*. Along *BC* an energy switch (predissociation) occurs from the carbonyl group to the C–C link, *via* the common carbon atom. At *C*, the molecule may *either* decompose by the rupture of the C–C link, *or* it may be "internally" stabilised along *CD* by partial absorption of energy into other degrees of freedom as described above.

FIG. 4.



It is thus apparent that with a polyatomic molecule, light may be absorbed in a region of continuous absorption without disruption, the net effect being an internal degradation of the energy to heat. It is probable that many examples will come to light of polyatomic molecules with diffuse spectra which show only low photochemical efficiency.

When a quantum of light is absorbed in the long-wave region of the absorption band, the acetone molecule will persist for an interval in the excited state, and at the end of about $10^{-8}$ sec. will, if nothing else happens, remit the energy as fluorescence. Even in the region of discrete absorption there is, however, a finite probability of a radiationless transition to the unstable C–C level, and this will increase with the magnitude of the absorbed quantum. As we have seen, molecules undergoing this transition may or may not ultimately decompose, but the possibility of fluorescence is lost. The chance of decomposition further increases with the energy of the quantum, since in these circumstances stabilisation becomes increasingly more and more difficult.

With acetone in the spectral region of discrete structure, it is apparent that while some molecules fluoresce, others decompose: there is thus a dual probability, which must be conditioned by the internal state of the molecule, after the manner suggested by Franck, Sponer, and Teller (*Z. physikal. Chem.*, 1932, **18**B, 88). In the continuous region, however, the predissociation switch occurs in all cases, within the period of a free vibration ($10^{-10}$ sec.), and there is no fluorescence. The two regions merge slowly into one another, resulting in a region of overlap, or " diffuse " threshold of photochemical activity. In view of the process of internal thermal degradation which we described above, it is now clear why Damon and Daniels, in spite of the low quantum efficiency of 0·4, were only able to account for 3% of the absorbed energy in the fluorescence radiation. The deficiency represents the energy which is degraded internally to heat.

*Conclusion.*—Coupled with the evidence yielded by the photodecomposition of the unsymmetrical ketone, methyl ethyl ketone, we may therefore conclude, on the basis of the above evidence, that the primary decomposition of acetone occurs by way of free radicals: $CO(CH_3)_2 = CO + 2CH_3 - 80$ kg.-cals. As has been previously observed, it is impossible to state whether these radicals are detached simultaneously, or the one followed rapidly by the other. The radicals then combine to give the ethane which is found as a principal product of the decomposition. We have seen that, even in the region of continuous absorption, this process is not completely efficient, but that often molecules in a state of predissociation may degrade their energy to heat instead, through a process of internal stabilisation.

## SUMMARY.

(1) The absorption spectrum of acetone has been shown to consist of two parts: (*a*) a region of discrete absorption extending from 3340 to *ca.* 2950 Å., and (*b*) a region of continuous absorption, completely devoid of structure, extending from *ca.* 3000 to 2200 Å. These two regions overlap somewhat.

(2) The fluorescence of acetone vapour has been studied by visual and photographic means. It increases in intensity as the pressure of acetone is increased up to 180 mm., and is not appreciably affected by inert gases. Its intensity is diminished and its colour changed by oxygen, as recorded by Damon and Daniels. This is probably due to the specific reaction of excited acetone molecules with oxygen, and to the production of a second (transient) fluorescent substance.

(3) A region of infra-red absorption lying between 7000 and 10,000 Å., inferred from the measurements on the fluorescence, has been verified.

(4) It has been shown that fluorescence is stimulated only by absorption in that part of the spectrum showing discrete structure. Absorption in the continuous part of the spectrum gives no fluorescence at all.

(5) The main products of photodecomposition of acetone are carbon monoxide and ethane, together with a small amount of methane.

(6) Photodecomposition occurs both in the region of fine structure and in the continuum. The quantum efficiency at $\lambda = 3150$ is 0·2, and at $\lambda = 2650$ it is 0·4, in agreement with the results of Damon and Daniels.

(7) It is inferred that the decomposition does not involve the bimolecular reaction of excited molecules, but that primary dissociation occurs to give free hydrocarbon radicals and carbon monoxide. The radicals combine to give ethane.

(8) Even in the region of continuous absorption this process is quite inefficient, and it is shown that a polyatomic molecule in a state of predissociation may degrade its energy to heat instead of decomposing. This occurs through a process of " internal " stabilisation.

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