# **106.** *The Photodecomposition of Gaseous Acetone. Part II.*

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It has been shown that the apparently contradictory results of Herr and Noyes (*J. Amer. Chem. Soc.*, 1940, **62**, 2052) and of Spence and Wild (J., 1937, 352) on the photodecomposition of gaseous acetone in the " continuum " region of absorption can be represented by a single expression derived from a common mechanism. Attention has been directed to a number of interesting facts relating to the photodecomposition in the banded region of absorption which are inexplicable on the basis of a purely radical type of mechanism. A theory which postulates two activated states of the acetone molecule, one of which has a life period of the order of $10^{-8}$ sec. and the other of which is a metastable state of long life (*ca.* $10^{-2}$ sec.), has been advanced in order to account for these results.

WE have already shown (J., 1937, 352) that the photodecomposition of gaseous acetone is a complex process, and that the reaction at room temperature could be represented stoicheiometrically by the equation $(2y - x)\mathrm{COMe_2} + h\nu \longrightarrow y\mathrm{C_2H_6} + x\mathrm{CO} + (y - x)(\mathrm{COMe})_2$, the actual values of $x$ and $y$ depending on the conditions. Increase of light intensity in the " continuum " region of absorption (2537 A.) caused the ratio $C_2H_6/CO$ to increase towards a maximum value of 3 for an acetone pressure of 160 mm., and a mechanism was advanced which yielded an expression for the ratio in good agreement with the experimental results. In the region of banded absorption (3130 A.), however, the value of the ratio appeared to be considerably lower than that predicted by the theory, being approximately unity. It was suggested that absorption of light of wave-length 3130 A. by acetone results in the production of an excited molecule which ultimately dissociates directly into carbon monoxide and ethane rather than into radicals as in the " continuum ". This mechanism was also applied to account for the unusual results obtained with mixed light. In this case, the $C_2H_6/CO$ ratio increased to a maximum value of about 2 and then decreased with increase of light intensity. Such a decrease in the ratio could be brought about if acetyl radicals produced by the " continuum " light were decomposed into $CH_3$ and CO on colliding with the excited acetone molecules of long life resulting from absorption of light of wave-length 3130 A.

Although the evidence in favour of the proposed primary process for the " continuum " region ($\mathrm{COMe_2} \xrightarrow{h\nu} \mathrm{CH_3} + \mathrm{CH_3{\cdot}CO}$) was strong enough to bring about its general acceptance, this was not true of the mechanism for the banded region. Further experiments have been carried out, therefore, with the object of confirming our previous results. It is now possible, moreover, to carry the analysis of the whole reaction a stage further in view of a recent paper by Herr and Noyes (*J. Amer. Chem. Soc.*, 1940, **62**, 2052) in which accurate data are given for monochromatic light of wave-lengths 2536 A. and 3130 A. Before these results can be compared with our own, however, it is necessary to express them in the same units. Both sets of data have been correlated, therefore, by plotting the ratio $C_2H_6/CO$ against rate of decomposition expressed as c.c. of acetone vapour decomposed per hour per c.c. of reaction space. In the case of Herr and Noyes's data this rate can be obtained from the expression : rate of decomposition $= \Phi \times I_{\text{abs.}}$, where $\Phi$ is the quantum yield for acetone decomposition as given in their paper. The quantum yield appears to be independent of $I_{\text{abs.}}$ except at very low intensities, where a slight increase is observed. Our previous result that the rate of decomposition is proportional to intensity over a forty-fold range is in agreement with this (*loc. cit.*, p. 357). There is an inconsistency between the quantum yields given in Fig. 6 and Figs. 5 and 7 of Herr and Noyes's paper. Values of the rate of acetone decomposition, $D$, have been calculated on the basis of Figs. 5 and 7.

The data have not been corrected for temperature, since its effect on the ratio is small in this region.

TABLE I.

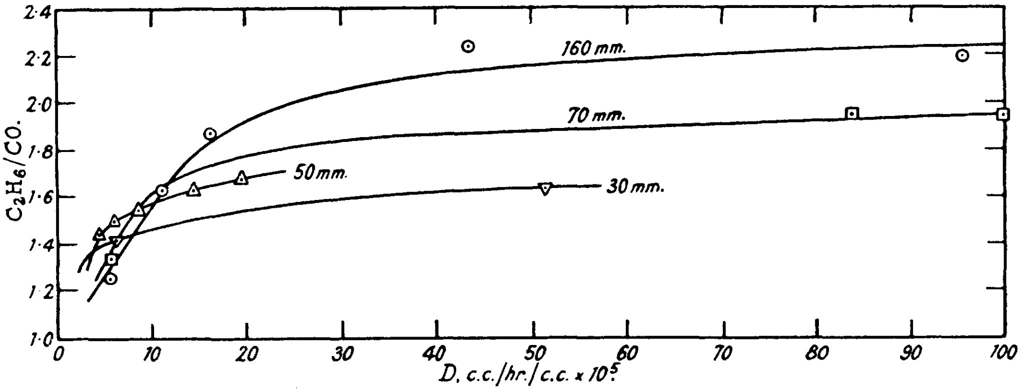
*Photodecomposition in the Region of Continuous Absorption.*
*Influence of Light Intensity and Acetone Pressure.*

| Authors. | $COMe_2$, mm. | Temp. | D, c.c./hr./c.c. × $10^5$. | $C_2H_6/CO$. Obs. | Calc. |
|---|---|---|---|---|---|
| S & W ........................ | 160 | 20·0° | 192 | 2·44 | 2·41 |
| ,, ........................ | ,, | 19·5 | 167 | 2·44 | 2·38 |
| ,, ........................ | ,, | 21·0 | 205 | 2·47 | 2·42 |
| ,, ........................ | ,, | 20·0 | 95·4 | 2·18 | 2·26 |
| ,, ........................ | ,, | 21·0 | 43·5 | 2·23 | 2·06 |
| ,, ........................ | ,, | 20·0 | 16·1 | 1·87 | 1·75 |
| ,, ........................ | ,, | 21·0 | 11·1 | 1·63 | 1·62 |
| H & N ........................ | ,, | 25·0 | 5·72 | 1·25 | 1·38 |
| S & W ........................ | 70 | 20·0 | 83·9 | 1·94 | 1·90 |
| ,, ........................ | ,, | 20·0 | 100·8 | 1·92 | 1·92 |
| H & N ........................ | ,, | 25·0 | 5·85 | 1·33 | 1·46 |
| ,, ........................ | 50 | ,, | 4·59 | 1·45 | 1·41 |
| ,, ........................ | ,, | ,, | 5·11 | 1·5 | 1·43 |
| ,, ........................ | ,, | ,, | 8·68 | 1·55 | 1·52 |
| ,, ........................ | ,, | ,, | 14·3 | 1·63 | 1·60 |
| ,, ........................ | ,, | ,, | 19·5 | 1·68 | 1·64 |
| S & W ........................ | 32 | 20·0 | 51·5 | 1·62 | 1·59 |
| H & N ........................ | 30 | 25·0 | 6·25 | 1·42 | 1·43 |

When the results are plotted (Fig. 1), the apparently contradictory facts that in Herr and Noyes's experiments the ratio decreased with rise of acetone pressure whilst in our experiments it did the reverse, become related by a family of curves.

FIG. 1.

*Variation of* $C_2H_6/CO$ *ratio with rate of photodecomposition of* $COMe_2$ *by continuum light.*



*Experiments in the Banded Region of Absorption.*—Acetone, dried and purified as described in our previous paper, was contained in a Pyrex glass tube connected to the quartz reaction vessel by a glass ventil (Bodenstein, *Z. physikal. Chem.*, 1930, *B*, **7**, 387). The reaction vessel was of the annular type, about 10 cm. long and having *ca.* 1 cm. between the walls of the annular reaction space, the volume of which was 155 c.c. Illumination was provided by a water-cooled mercury arc in Pyrex glass, similar to that described by Anderson and Burg (*J. Chem. Physics*, 1938, **6**, 586), consuming 12 amps. from a 110-volt supply. The arc was mounted vertically so as to pass through the centre of the reaction vessel coincident with its principal axis. A cylindrical reflector of polished aluminium surrounded the vessel in order to obtain maximum light intensity. After an experiment, the gases were pumped through a trap at −160° *via* a second glass ventil by means of a mercury pump. The carbon monoxide and ethane thus collected were transferred to the micro-gas analysis apparatus recently described by one of us (Spence, J., 1940, 1300). Carbon monoxide was determined by combustion over oxidised copper wire at

270°, and ethane by combustion over copper oxide–iron oxide at 600°. Finally, the carbon dioxide produced was absorbed over solid potassium hydroxide. Direct tests (nickel dimethylglyoxime reaction) on the condensate collected in the trap from six experiments failed to reveal the presence of diacetyl. The test was not sufficiently sensitive, however, to detect the presence of traces of diacetyl which might be formed at $C_2H_6/CO$ ratios only slightly greater than unity. Data from these experiments and from our previous paper, together with the results of Herr and Noyes (*loc. cit.*), are shown in Table II.

TABLE II.

*Photodecomposition in the Region of Banded Absorption.*
*Influence of Light Intensity and Acetone Pressure.*

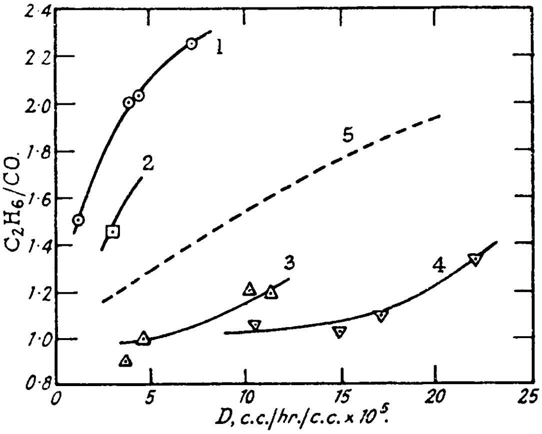
*d* = mean displacement of molecules from walls.

| Authors. | $COMe_2$, mm. | Temp. | Time, mins. | *D*, c.c./hr./c.c. × $10^5$. | $C_2H_6/CO$, obs. | *d*, cm. |
|---|---|---|---|---|---|---|
| S & W, 1941 ............... | 150 | 16° | 45 | 22 | 1·33 | 0·25 |
| ,, ............... | 150 | 16 | 45 | 17·2 | 1·09 | ,, |
| ,, ............... | 157 | 18 | 50 | 15·0 | 1·03 | ,, |
| ,, ............... | 123 | 21 | 30 | 10·4 | 1·05 | ,, |
| S & W, 1937 ............... | 164 | 19·5 | 2880 | 11·36 | 1·19 | 0·6 |
| ,, ............... | 164 | 20·5 | 2760 | 10·1 | 1·2 | ,, |
| ,, ............... | 161 | 20·5 | 1440 | 4·63 | 1·0 | ,, |
| ,, ............... | 160 | 19·5 | 4230 | 3·65 | 0·89 | ,, |
| H & N ..................... | 162 | 25 | 180 | 2·93 | 1·45 | 1·0 |
| ,, ..................... | 107 | ,, | 272 | 3·46 | 1·67 | ,, |
| ,, ..................... | 50 | ,, | 240 | 7·2 | 2·25 | ,, |
| ,, ..................... | 50 | ,, | — | 4·39 | 2·03 | ,, |
| ,, ..................... | 50 | ,, | — | 3·95 | 2·0 | ,, |
| ,, ..................... | 50 | ,, | — | 1·23 | 1·5 | ,, |
| ,, ..................... | 25·5 | ,, | 291 | 5·05 | 2·63 | ,, |
| ,, ..................... | 23 | ,, | 240 | 5·19 | 2·71 | ,, |
| ,, ..................... | 12·3 | ,, | 240 | 6·52 | 3·49 | ,, |

Our experiments were at first regarded simply as confirmatory of the earlier results in the banded region until the publication of apparently contradictory results by Herr and Noyes obliged us to reconsider the whole problem. Although we have been unable to carry out any further experimental work in this field, the existing data (Table II and Fig. 2) permit us to draw

FIG. 2.

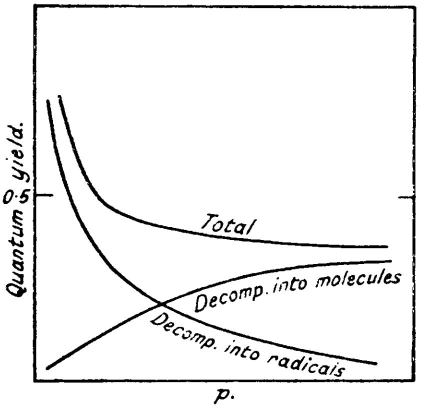
*Variation of* $C_2H_6/CO$ *ratio with rate of photodecomposition of* $COMe_2$ *by light in the banded region.*



1. 50 *mm.* $COMe_2$, d = 1 *cm.*
2. 160 ,, ,, d = 1 *cm.*
3. ,, ,, ,, d = 0·6 *cm.*
4. ,, ,, ,, d = 0·25 *cm.*
5. ,, ,, ,, *continuum curve.*

FIG. 3.

*Variation of quantum yield of photodecomposition of* $COMe_2$ *with pressure in the banded region (qualitative).*



a number of definite conclusions. In general, there appears to be an increase in the $C_2H_6/CO$ ratio with decrease of acetone pressure in a given vessel, and for moderate acetone pressures, in a series of different vessels, reduction in the mean distance of molecules from the wall causes the ratio to approach a value of unity.

## DISCUSSION.

In our previous communication (*loc. cit.*) we showed that the primary process in the photodissociation of gaseous acetone at room temperatures, by " continuum " light, is $COMe_2 \xrightarrow{h\nu} CH_3 + CH_3{\cdot}CO$. Furthermore, a mechanism was advanced, based on reasonable premises, which accounted for the experimental results with considerable accuracy. Although the reasons for the various steps of the mechanism still remain valid, certain modifications must now be introduced if the data given in Table I are to be accounted for. In the following scheme, the individual reactions have been given the same numbers as before in order to avoid confusion.

(1) $(CH_3)_2CO + h\nu \longrightarrow CH_3 + CH_3{\cdot}CO$
(2) $2CH_3 \longrightarrow C_2H_6$
(3) $2CH_3{\cdot}CO \longrightarrow (CH_3{\cdot}CO)_2$
(4*a*) $CH_3 + CH_3{\cdot}CO \longrightarrow (CH_3)_2CO$
(4*b*) $CH_3 + CH_3{\cdot}CO \longrightarrow C_2H_6 + CO$
(5) $CH_3{\cdot}CO + M \longrightarrow CH_3 + CO + M$

Reactions (2), (3), and (4*a*) must actually occur by the mechanism

$$CH_3 + CH_3 \underset{k_b}{\overset{k_f}{\rightleftharpoons}} C_2H_6^*$$

$$C_2H_6^* + M \xrightarrow{k_s} C_2H_6 + M$$

where M represents a third entity which brings about the stabilisation of the excited molecule. This gives $k_2 = k_f \,.\, k_s[M]/(k_b + k_s[M])$. When the lifetime of $C_2H_6^*$ is short, $k_b \gg k_s[M]$, and hence $k_2 = k_f \,.\, k_s[M]/k_b$. On the other hand when the lifetime of $C_2H_6^*$ is long, $k_2 = k_f$. Our results, however, point to a state of affairs between these two extremes where, in a manner analogous to the Freundlich equation, we can put $k_2 = k_2'[M]^x$.

There is now considerable evidence to indicate that the quantum yield of the primary process in the " continuum " region is unity, and that the low total quantum yield actually observed is due to recombination (cf. Gorin, *J. Chem. Physics*, 1939, **7**, 256). Reaction (4*a*) has therefore been introduced to take account of recombination. The decomposition of the acetyl radical, reaction (5), has also become pressure-dependent in the new scheme in order to account for the increase of $C_2H_6/CO$ with fall of pressure at low intensities (Fig. 1). The smaller the value of $k_5$, the lower the intensity at which this effect becomes operative. It is noteworthy that the same reaction has been found necessary to explain pressure effects in the photolysis of acetaldehyde (Blacet and Volman, *J. Amer. Chem. Soc.*, 1938, **60**, 1243).

If we suppose that the concentrations of methyl and acetyl radicals are stationary and that $k_2$ and $k_3 \gg k_5$ [reactions (2) and (3) do not require energy of activation whereas several workers have assigned an activation energy of about 18 kg.-cals. to reaction (5)], we obtain $[CH_3{\cdot}CO] = \sqrt{k_2/k_3}[CH_3]$ and therefore

$$\frac{C_2H_6}{CO} = \frac{1 + \sqrt{k_2k_3}/k_{4b}}{1 + \dfrac{k_5}{k_{4b}}[M]\sqrt{\dfrac{2k_2 + \sqrt{k_2/k_3}(k_{4a} + k_{4b})}{I_{abs.}}}}$$

Now

$$D = -\frac{d[COMe_2]}{dt} = I_{abs.}\,\frac{2k_2 + k_{4b}\sqrt{k_2/k_3}}{2k_2 + \sqrt{k_2/k_3}(k_{4a} + k_{4b})}$$

or $D = I_{abs.} \times \Phi_{COMe_2}$, where

$$\Phi_{COMe_2} = (2k_2 + k_{4b}\sqrt{k_2/k_3})/[2k_2 + \sqrt{k_2/k_3}(k_{4a} + k_{4b})].$$

The mechanism predicts that **Φ** will decrease slowly with rise of pressure. At moderate or high intensities, the quantum yield will be independent of intensity, but at very low intensities $\Phi$ will increase somewhat owing to the increasing importance of reaction (5). These deductions are in agreement with the experimental results of Herr and Noyes.

Substituting for $I_{\text{abs.}}$, we have

$$\frac{\text{C}_2\text{H}_6}{\text{CO}} = \frac{1 + \sqrt{k_2k_3}/k_{4b}}{1 + \frac{k_5}{k_{4b}}[\text{M}\sqrt{\frac{2k_2 + k_{4b}\sqrt{k_2/k_3}}{D}}}$$

Since the value of $x$ in the expression $k_2 = k_2'[\text{M}]^x$ is found (from the experimental data) to be approximately 0·5, the terms under the square root sign will yield only a low power of [M] and can be regarded therefore as approximately constant. After collection of constants, and substitution of $p$ for [M], we obtain $\text{C}_2\text{H}_6/\text{CO} = (1 + k_1p^x)/(1 + k_2p/\sqrt{D})$. The calculated values of $\text{C}_2\text{H}_6/\text{CO}$ given in Table I have been obtained from this equation, appropriate values being used for $k_1$, $k_2$, and $x$, *viz.*,

$$\text{C}_2\text{H}_6/\text{CO} = (1 + 0{\cdot}1p^{0{\cdot}57})/(1 + 5 \times 10^{-5}p/\sqrt{D})$$

where $p$ is expressed in mm. of mercury and $D$ in c.c./hr./c.c. of reaction space.

Herr and Noyes (*loc. cit.*) have suggested a mechanism based on diffusion, which is in accord with their results obtained over a narrow range of rather low intensities. When the experiments at higher intensities are considered, however, *viz.*, in the region where $\text{C}_2\text{H}_6/\text{CO}$ increases with increase of acetone pressure, the mechanism becomes untenable.

The situation as regards the banded region of absorption is more obscure. Nevertheless, if due weight is given to the existing data, certain conditions emerge, to which any selected theory must conform. These are briefly as follows. (*a*) At constant $I_{\text{abs.}}$: the quantum yield and $\text{C}_2\text{H}_6/\text{CO}$ decrease with increase of pressure. This effect is much more pronounced than in the short-wave region and the data suggest that the quantum yield approaches unity as $p \to 0$. (*b*) At constant pressure : the quantum yield is independent of $I_{\text{abs.}}$, in contrast to its behaviour in the "continuum" region. On the other hand, $\text{C}_2\text{H}_6/\text{CO}$ increases with increase of intensity as in the "continuum" region. (*c*) Influence of the wall : At moderate pressures (160 mm.), a reduction in the mean molecular distance from the wall by the use of narrower vessels causes $\text{C}_2\text{H}_6/\text{CO}$ to decrease towards unity. This effect would also be expected to become noticeable when the pressure is reduced in any given vessel, but actually, the ratio increases rapidly with fall of pressure. (*d*) Effect of mixed light : At high intensities, the $\text{C}_2\text{H}_6/\text{CO}$ value obtained with "continuum" light alone is reduced by the presence of light in the banded region to an extent which is considerably greater than would be expected on a purely additive basis (Spence and Wild, *loc. cit.*). It does not seem to be possible to account for these results on the basis of radical mechanism alone and the only alternative is a mechanism involving active molecules.

There is now a good deal of evidence from other sources pointing to the existence of excited acetone molecules of long life. The yellow-green fluorescence exhibited by acetone under the influence of ultra-violet light is now known to be due to a sensitised fluorescence of diacetyl formed during the reaction (Almy *et al.*, *J. Chem. Physics*, 1940, **8**, 37, 805), and arises from a transference of energy from excited acetone molecules to diacetyl. Although this fluorescence is present at all wave-lengths in the absorption band, it is most pronounced towards the long-wave end ($\lambda > 2800$ A.; Norrish, Crone, and Saltmarsh, J., 1934, 1456). The effect increases towards a maximum value with time and becomes measurable after 5 mins. from the start of illumination. Although we were unable to detect the presence of diacetyl in our experiments at 160 mm. (Table II), the high values of $\text{C}_2\text{H}_6/\text{CO}$ found by Herr and Noyes indicate that considerable amounts must be formed at lower pressures, and the fluorescence work shows that traces of diacetyl must be present under all conditions. It follows, therefore, that there must be some radical production in the long-wave region, since diacetyl can only be formed by the combination of two acetyl radicals. Again, since the partial pressure of diacetyl which can be built up after 5 mins.' illumination must be extremely small, it follows that the excited acetone molecules concerned in the transference of energy to diacetyl are comparatively long-lived. This result is consistent with the observations in mixed light (condition *d*) and with the influence of diameter at high pressures (condition *c*). Some idea of the life period involved can be obtained from a consideration of the diameter effect (Table II). When the mean displacement of the molecules from the wall is reduced from 1 cm. to 0·25 cm., $C_2H_6/CO$ is reduced from 1·45 to about unity for 160 mm. acetone pressure. At this pressure, the time required to diffuse 1 cm. is about 0·1 sec. and for 0·25 cm. about $5 \times 10^{-3}$ sec. A mean life period of about $10^{-2}$ sec. for the excited acetone molecule would therefore be in accord with the effect of change of diameter, with the effect of mixed light, and with the fluorescence results.

The effect of increase of pressure on the quantum yield and on $C_2H_6/CO$ (condition *a*), however, could not possibly be accounted for on this basis. If the effect were due to deactivation of an excited molecule by collisions, such as we have in unimolecular reactions, a life-period of about $10^{-8}$ sec. would be expected. We have been able to reconcile these widely different requirements in the following manner. It is assumed that on absorption of light of wave-length 3130 A., an excited acetone molecule is produced which, if left to itself, executes a complicated vibrational motion on the energy hypersurface of the excited state and ultimately decomposes into free radicals. Alternatively, the cause of decomposition may be a transition to another repulsive energy surface, but the evidence does not permit us to distinguish between the two possibilities. The fact that the absorption spectrum at 3130 A. shows some structure indicates that the time between activation and decomposition must be considerably greater than the period of a single vibration (*ca.* $10^{-13}$ sec.). When the acetone pressure is raised, however, the excited molecule suffers an increased number of collisions with loss of energy and may change to a metastable state, which no longer yields radicals but either reverts to the normal state or decomposes, perhaps by induced predissociation, into ethane and carbon monoxide after a time interval of the order of $10^{-2}$ sec.

The quantum yield decreases from unity with increase of pressure in such a manner as to suggest that the life-period of the first excited state is about $10^{-8}$ sec. However, the curve does not follow a simple deactivation formula, since the number of metastable molecules yielding ethane and carbon monoxide must increase with increase of pressure, so that the experimental curve represents the sum of two effects (Fig. 3). The reactions can be represented as follows :

$$(6)\quad (CH_3)_2CO + h\nu \longrightarrow (CH_3)_2CO' \qquad (8a)\quad (CH_3)_2CO'' \xrightarrow{10^{-2}\text{ sec.}} C_2H_6 + CO$$

$$(7a)\quad (CH_3)_2CO' \xrightarrow{10^{-8}\text{ sec.}} CH_3 + CH_3{\cdot}CO \qquad (8b)\quad (CH_3)_2CO'' \longrightarrow (CH_3)_2CO$$

$$(7b)\quad (CH_3)_2CO' + M \longrightarrow (CH_3)_2CO'' + M \qquad (8c)\quad (CH_3)_2CO'' \xrightarrow{\text{wall}} C_2H_6 + CO$$

It follows from this mechanism that at low pressures decomposition into radicals predominates and $C_2H_6/CO$ can attain high values, whilst at pressures exceeding 100 mm., direct decomposition into ethane and carbon monoxide is the main primary process. The effect of increase of intensity on the quantum-yield will be small, especially at the higher pressures where the proportion of radical decomposition is much reduced (*cf.* condition *b*). If the metastable molecule diffuses to the wall and is there decomposed into saturated molecules (reaction 8*c*), the influence of diameter can be understood.

Herr and Noyes (*loc. cit.*) found that the $C_2H_6/CO$–acetone pressure curve for 3130 A. lay above that for 2537 A., *i.e.*, that the value of $C_2H_6/CO$ for a given pressure was greater for the long- than for the short-wave light. They suggested, by way of explanation, that as the wave-length is reduced, an increasing proportion of the acetone molecules break up into three radicals, *viz.*, $(CH_3)_2CO \xrightarrow{h\nu} CH_3 + CH_3 + CO$, owing to the spontaneous decomposition of the energy-rich acetyl radicals produced in the first instance. In our view, the excess vibrational energy possessed by the acetyl radicals would be rapidly dissipated by collision at high pressures, but with decrease of pressure a growing proportion would decompose spontaneously. In consequence, the concentration of acetyl radicals and therefore the value of $C_2H_6/CO$ would be less in the " continuum " region than in the banded region at low pressures, in agreement with the experimental results.

As regards the effect of mixed light (*cf.* condition *d*), the explanation advanced in our previous paper, *viz.*, that excited acetone molecules of long life produced in the banded region bring about the decomposition of acetyl radicals produced in the " continuum " region, still remains valid :

$$(9)\ (CH_3)_2CO'' + CH_3{\cdot}CO \longrightarrow (CH_3)_2CO + CH_3 + CO$$

Both the quantum yield and $C_2H_6/CO$ tend to unity with rise of temperature. In the " continuum " region, since reactions (4*b*) and (5) require energy of activation, they will become increasingly important at higher temperatures, causing a reduction in the concentration of free acetyl radicals. The quantum yield will accordingly rise and $C_2H_6/CO$ will fall, both approaching unity as the temperature rises. In the case of the banded region, there is an additional effect to be considered. The energy associated with light of wavelength 3130 A. corresponds closely with recent estimates of the strength of the carbon–carbon bond, *viz.*, about 90 kg.-cals. per mol. As the temperature rises, the ground state will possess higher vibrational energy, and upon absorption of a light quantum, a point on the upper energy surface will be reached from which radical decomposition is more readily achieved. The life-period of acetone molecules will be shorter, deactivation will become less probable, and at temperatures above 100° there may be no difference between the primary processes occurring in the two regions of absorption (*cf.* Leermakers, *J. Amer. Chem. Soc.*, 1934, **56**, 1899 ; Gorin, *loc. cit.*).

It is realised that the theory now advanced is a complicated one, but each phase of it has been related to some definite experimental result. More work is required covering a wide range of pressures and intensities in both absorption regions under standard experimental conditions. The theory suggests that the addition of foreign gases should have a marked effect on the reaction, and it is also a consequence of the theory that decrease of vessel diameter should result in an increase in the quantum yield in the banded region. These points are open to experimental confirmation. Refinements, such as the reversibility of reaction (7*b*) for instance, have been omitted, and no attempt has been made to apply the theory of the banded region quantitatively.

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