

[CONTRIBUTION FROM THE METCALF CHEMICAL LABORATORY OF BROWN UNIVERSITY]

Photochemical Studies. XXIII. The Photochemical Decomposition of Acetone Vapor near 1900 Å. A Comparison with the Decomposition at Longer Wave Lengths

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Acetone, in common with other ketones and aldehydes, exhibits an absorption region beginning at wave lengths somewhat longer than 3000 Å. and extending down to about 2200 Å. On the long wave end some structure has been noted² and fluorescence has been observed in this region.³ Whether or not fluorescence is excited by wave lengths below those for which discrete structure is obtained seems to be the object of some disagreement.⁴

It seems generally agreed that the main products of photochemical decomposition in this near ultraviolet region of the spectrum are carbon monoxide and ethane, although small amounts of other substances may be formed.^{4a,5} The quantum yield is a function of wave length, increasing slightly as the wave length is decreased. While the general aspects of the photochemical decomposition of acetone in this region of the spectrum seem quite well established, experiments have not been carried out over a sufficient range of intensities, pressures of acetone and pressures of foreign gas to make it possible to present a mechanism free from criticism.

Recently the ultraviolet absorption spectrum of acetone has been investigated.^{2c} In addition to the absorption region near 3000 Å., one additional region is susceptible of investigation with apparatus made of quartz. This region consists of discrete bands extending from about 1995 to about 1820 Å., probably overlaid with a faint continuum. Manning⁶ has developed a method of

gas analysis applicable to the products of acetone decomposition and studied the gases produced upon illuminating acetone vapor with polychromatic radiation transmitted by fluorite.

A complete understanding of the photochemistry of acetone can be based only on a thorough study of as many different excited states as possible over a wide range of experimental conditions. It is for this reason that the present investigation at wave lengths near 1900 Å. was carried out. A consistent picture of the results is possible.

I. Experimental Procedure and Results

The following primary processes and subsequent steps are possible in any dissociation such as that of acetone (I represents quanta absorbed per second, A represents an acetone molecule, A_1 represents an excited acetone molecule, D represents dissociation products, M represents a molecule of foreign gas):

Reaction	Rate	
$A + h\nu = D;$	I_1	(1)
$A + h\nu = A_1;$	I_2	(2)
$A_1 = A + h\nu_1;$	$k_1(A_1)$	(3)
$A_1 = A_2;$	$k_2(A_1)$	(4)
$A_1 = D;$	$k_3(A_1)$	(5)
$A_1 + A = 2A;$	$k_4(A_1)(A)$	(6)
$A_1 + A = D + A;$	$k_5(A_1)(A)$	(7)
$A_1 + M = A + M_1;$	$k_6(A_1)(M)$	(8)
$A_1 + M = D + M;$	$k_7(A_1)(M)$	(9)

If it can be shown that the dissociation products, D , do not react with each other to reform acetone, the quantum yield, ϕ , is found to be

$$\phi = (I_1/(I_1 + I_2)) + (I_2/(I_1 + I_2))(k_3 + k_5(A) + k_7(M))/(k_1 + k_2 + k_3 + (k_4 + k_5)(A) + (k_6 + k_7)(M)) \quad (10)$$

providing the molecule A_2 either does not dissociate or has a very long life. The quantities in parentheses may be expressed either in pressure units or in numbers of molecules per cubic centimeter.

attempt was made to remove mercury resonance radiation. In the present article it is shown that the effect of the latter is quite appreciable, particularly at low acetone pressure. Also Duncan [*J. Chem. Phys.*, **3**, 131 (1935)] has shown that acetone absorbs strongly still shorter wave lengths which would be transmitted by fluorite. In view of these facts the results of Manning, which generally showed relatively large amounts of hydrogen to be produced, should not be viewed as being in disagreement with the results reported in the present article.

(1) Jesse Metcalf Fellow, 1935-1936.

(2) This structure seems to have been observed first by Herzberg, see (a) Scheibe, Povenz and Linström, *Z. physik. Chem.*, **B20**, 297 (1933), for mention. It has been confirmed subsequently by other workers: (b) Crone and Norrish, *Nature*, **132**, 241 (1933); (c) Noyes, Duncan and Manning, *J. Chem. Phys.*, **2**, 717 (1934).

(3) Norrish, *Nature*, **133**, 837 (1934).

(4) (a) Damon and Daniels, *THIS JOURNAL*, **55**, 2363 (1933); (b) Fisk and Noyes [*J. Chem. Phys.*, **2**, 654 (1934)] have studied the fluorescence excited by monochromatic 3130 Å. radiation of mercury. They found the fluorescence to follow a Stern-Volmer mechanism at the pressures used (50 to 190 mm.). They did not investigate the effect of wave length. Recently Mr. Fisk and one of us (J. P. H.) using a crystal quartz monochromator and a quartz capillary arc have observed fluorescence to be produced by all of the mercury lines from 3130 to 2536 Å., but apparently not by the weak lines at still shorter wave lengths. These results are in agreement with those of Damon and Daniels.

(5) Norrish, Crone and Saltmarsh, *J. Chem. Soc.*, 1456 (1934).

(6) Manning, *THIS JOURNAL*, **56**, 2589 (1934). Monochromatic radiation was not used in Manning's experiments and moreover no

The detailed description of the effect of radiation on the acetone molecule involves, therefore, the proof that the dissociation products do not reunite to give acetone, decision as to whether step (1) or step (2) or both must be considered, the evaluation of the constants k_1 - k_7 and decision as to the nature of the molecule, A_2 .

(a) The Nature of the Absorption Process.—

The source of radiation used in these experiments was a spark between slowly revolving aluminum disks excited by two 1-kva. 25,000-volt transformers connected in parallel. The method of focal isolation was used to obtain monochromatic radiation and the purity of the radiation was tested spectroscopically using a small fluorite prism spectrograph. The following lines were transmitted with sufficient intensity to be photographed: 1854.7, 1858.2, 1862.5, 1862.9, 1930.3, 1935.2, 1989.8. The following bands lie near these exciting lines (intensities in parentheses):^{2c} 1866.7 (3), 1868.9 (6), 1870.3 (3), 1872.4 (6), 1921.1 (4), 1923.0 (3), 1925.3 (3), 1926.4 (3), 1927.2 (4), 1938.9 (6), 1939.8 (6), 1941.1 (6), 1942.1 (6), 1943.9 (6). Only bands lying within 10 Å. of an exciting line have been listed. These bands have quite sharp edges, indicating the possibility that rotational structure might be observed with sufficient resolution. No bands lie very close to the group of lines 1854.7-1862.9; moreover these lines are relatively weak from the source due to the absorption by quartz and by the relatively long air path. The 1989.9 line falls in a region in which acetone is quite transparent. Most of the absorption must be due to the two lines at 1930.3 and 1935.2 Å.

In addition to the above lines this type of spark emits a faint continuum which cannot be ignored since it leads to some excitation of mercury vapor to the 2^1P_1 state through absorption of the 1849 Å. line. After this effect was discovered a chamber practically free from air circulation and containing mercury vapor was inserted between the second lens and the reaction vessel. This produced a noticeable decrease in the amount of decomposition at low acetone pressures and the evidence indicated convincingly that this error was removed in this way. The absorption coefficient of the 1849 line by mercury vapor is exceedingly high and even a temperature of -77° does not remove mercury vapor well enough to prevent practically complete absorption in the path length used.

Since absorption takes place in a banded region overlaid with a faint continuum, the spectroscopic evidence might indicate that both equations (1) and (2) should be considered. However, as will be shown, the data indicate that a molecule with a relatively long life is produced and that hence equation (1) may be omitted from consideration.

The fraction of the radiation absorbed by the acetone was determined by means of a photoelectric cell with quartz envelope. The following equation using two absorption coefficients was found to be obeyed (see Table I).

$$I/I_0 = 0.868 \exp. (-0.975P) + 0.132(1 - 0.0114P) \quad (11)$$

(I = transmitted intensity, I_0 = incident intensity, P is pressure in millimeters. The path length was 7.5 cm.)

TABLE I
ABSORPTION OF RADIATION BY ACETONE VAPOR

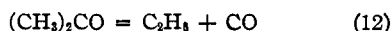
Pressure, mm.	I/I_0 calcd.	I/I_0 obsd.
0.295	0.786	0.791
.583	.627	.642
1.14	.422	.434
1.82	.281	.255
3.80	.149	.160
5.00	.132	.137
8.60	.122	.117
12.8	.113	.115
19.3	.103	.103

(b) Fluorescence.—A fluorescence cell was constructed with a window so placed that any fluorescence could be observed at right angles to the incident beam. Scattered and reflected radiation was reduced by tapering the ends of the tube and painting the entire cell except the windows with black paint. No visible fluorescence could be observed and attempts to produce blackening of ultraviolet sensitive plates gave negative results.^{4b} If fluorescence exists it must either be very weak or the emitted radiation must lie in a region of the spectrum which could not be detected by the methods used.

(c) The Determination of Quantum Yields.—

As shown by Manning⁸ at low acetone pressures (below 0.03 mm.) approximately one molecule of carbon monoxide is produced per molecule of acetone disappearing (the average ratio was 1.03). In the present experiments no hydrogen was found and at low acetone pressures, as shown in Table II, carbon monoxide constituted very nearly 50% of the gases produced during decomposition. There seems to be no doubt, therefore,

that the decomposition proceeds almost solely by the reaction



At higher acetone pressures some of the ethane seems to dissolve in the acetone upon condensation with liquid air, as found by Norrish and co-workers.⁵ The number of molecules of acetone disappearing is based, therefore, on an analysis for carbon monoxide.⁶

TABLE II
PERCENTAGE OF CARBON MONOXIDE IN REACTION PRODUCTS

Pressure of acetone, mm.	Total pressure of products, mm.	Carbon monoxide pressure, mm.	Carbon monoxide in products, %
1.80	0.0223	0.0110	49.8
1.78	.0210	.0102	48.7
8.35	.0191	.0098	51.3
Average			49.9

For determinations of the absolute values of the quantum yield a hydrogen bromide actinometer was used. For this the production of one molecule of hydrogen (uncondensed by liquid air) per absorbed quantum was assumed.⁷ The hydrogen bromide cell was about 15 cm. in length and pressures of hydrogen bromide of 10 to 15 mm. were employed. Under these conditions over 99% of the radiation was absorbed by the actinometer.

The hydrogen bromide cell was placed directly in back of the cell containing the acetone vapor, one window (of fused quartz sealed to the actinometer vessel) being in common between the two cells. The transmission of this window was measured subsequently after cutting off the end of the cell. The hydrogen bromide cell was made entirely of quartz and no wax was present in this system. The crystal quartz front window of the acetone cell was attached with picein wax.

In making a run the acetone was frozen with liquid air and the hydrogen bromide decomposition determined, a photoelectric cell being used to detect any variations in the over-all intensity of the spark. The acetone was then vaporized and the decomposition of the hydrogen bromide again determined. Corrections were made for variation in intensity between the two parts of the experiment. For this purpose the ultraviolet intensity was assumed to vary directly with the over-all intensity of the spark. This is not strictly true, but since intensity variations were always small the error introduced by the assumption would be negligible.

(7) Warburg, *Sitzber. preuss. Akad. Wiss.*, 314 (1916).

Table III presents the absolute values of the quantum yield as determined with the hydrogen bromide actinometer.

TABLE III
ABSOLUTE QUANTUM YIELDS OF ACETONE DECOMPOSITION

Acetone pressure, mm.	Time, min.	Quanta absorbed $\times 10^{-17}$	Molecules of CO produced $\times 10^{-17}$	Incident quanta per sec. $\times 10^{-18}$	Quantum yield, ϕ	Quantum yield, calcd. eq. (15)
6.00	120	2.19	1.163	4.19	0.53	0.57
2.20	38	0.605	0.361	4.87	.60	.61
2.20	60	1.57	.873	7.51	.56	.61
3.2	60	2.11	1.28	8.93	.61	.60
11.1	60	2.60	1.44	9.39	.56	.54
25.1	30	2.45	1.25	15.9	.51	.52

The complete determination of the mechanism of the decomposition involves the evaluation of the constants k_4 - k_7 . Quantum yields must be determined, therefore, with some precision over a wide range of experimental conditions and for this purpose the hydrogen bromide actinometer is not suitable. In particular the actinometer method lacks accuracy when the pressure of acetone is low and the percentage of the radiation absorbed small.

Relative quantum yields were obtained using a photoelectric cell to measure the incident intensity and calculating the amount of absorbed radiation from equation (11). A quantum yield of 0.55 at a pressure of 9.32 mm. (the average value at the average pressure in Table III) was assumed for the purpose of converting the relative quantum yields into absolute values. Table IV gives the values of the quantum yield obtained in this way.

TABLE IV
RELATIVE QUANTUM YIELDS OF ACETONE DECOMPOSITION

Acetone pressure, mm.	Intensity (arbitrary units)	Fraction absorbed	Pressure of CO, mm.	Time, min.	Quantum yield, ϕ	Quantum yield, calcd. eq. (15)
0.210	8.69	0.160	0.0072	180	0.66	0.64
.224	11.63	.169	.0094	180	.61	.64
.445	9.14	.296	.0092	120	.64	.64
1.07	10.19	.545	.0120	80	.62	.62
2.27	8.12	.784	.0102	60	.61	.61
4.20	1.59	.848	.00783	224	.59	.59
4.71	6.62	.858	.0086	60	.58	.58
4.73	8.85	.858	.0113	60	.57	.58
8.35	7.86	.873	.0097	60	.54	.56
8.35	7.70	.873	.0099	60	.56	.56
16.5	6.96	.894	.0088	60	.54	.53
20.4	11.38	.898	.0141	60	.53	.52
20.4	9.19	.898	.0115	60	.53	.52
52.3	9.35	.947	.0144	75	.50	.50
52.3	10.02	.947	.0159	90	.46	.50

(d) **The Effects of Added Gases.**—The constants k_6 and k_7 will be expected to vary from one

added gas to another. Three different gases were used: carbon dioxide, nitrogen and ethane. The experimental difficulties were least with the carbon dioxide which could be condensed with liquid air completely enough to permit easy removal of the decomposition products of acetone. This difficulty was particularly great with nitrogen and frequent circulation of the gases through the liquid air trap was necessary to remove all of the acetone vapor. Within experimental error none of these gases absorbed the radiation used. There is some slight possibility of decomposition of the ethane and carbon dioxide sensitized in some way by the acetone.

Table V shows the results obtained with added gases.

TABLE V
EFFECT OF ADDED GASES ON QUANTUM YIELD OF ACETONE DECOMPOSITION

Acetone pressure, mm.	Foreign gas pressure, mm.	Quantum yield	Quantum yield without added gas	Added gas
1.82	9.8	0.81	0.61	Carbon dioxide
1.81	9.8	.85	.61	
1.72	18.4	.88	.62	
2.12	2.23	.69	.61	Nitrogen
2.12	3.78	.81	.61	
2.34	7.38	.74	.61	Ethane
2.32	7.13	.75	.61	
2.30	12.30	.80	.61	

(e) **The Effect of Excited Mercury.**—The presence of excited mercury raised the apparent quantum yield as shown in Table VI. It is evident from the results that solid carbon dioxide-chloroform mixtures do not remove mercury vapor completely enough to prevent this effect.

TABLE VI
EFFECT OF EXCITED MERCURY ON APPARENT QUANTUM YIELD

Acetone pressure, mm.	Apparent quantum yield	Quantum yield, calcd. eq. (15)	Remarks
1.51	0.73	0.62	Resonance radiation present
0.155	.72	.65	Trap in CO ₂ -CHCl ₃
.124	.88	.65	
.134	.81	.65	
20.4	.53		Resonance radiation present
20.4	.53		Resonance radiation removed
9.9	.55	.55	Resonance radiation present

It is quite obvious from the results in Table VI that at high acetone pressures the fraction of the reaction due to excited mercury is too small to be significant. This is not true, as would be expected, at low pressures.

II. Discussion of Results

It is important first to show that the dissociation products do not react with each other to reform acetone. Two lines of evidence may be brought to bear on this point. (1) In Table III it is seen that the incident intensity was varied by a factor of nearly four and in Table IV the maximum variation is somewhat over seven-fold. In neither table is any significant variation of quantum yield with intensity apparent, whereas if a homogeneous gas phase recombination reaction were taking place the quantum yield should decrease as the intensity increases. (2) Methyl groups do not react with carbon monoxide, at least with any rapidity, when the carbon monoxide pressure is low and the temperature about 25°. This means that if two methyl groups and normal carbon monoxide are produced almost simultaneously, as Norrish suggests at longer wave lengths,⁵ the reverse reaction may be neglected. There still remains some slight possibility of a wall recombination between free radicals of the type of CH₃CO and CH₃. However, CH₃CO is probably not very stable and in the thermal decomposition of acetone its recombination with methyl groups does not seem to be important.⁹ The evidence against free radical recombination is, therefore, not conclusive but is about as good as one can ever obtain in a photochemical reaction.

In arriving at an equation which will express the quantum yield as a function of the various variables, it is necessary to decide whether the quantum yield approaches unity at zero pressure. Experiments were carried out at pressures down to 0.2 mm. and at this pressure the yield is far from one. Experimental difficulties prevented the execution of precise experiments at still lower pressures. However, it may be stated definitely that the mechanism outlined in equations (2) to (9) inclusive will lead to a quantum yield of unity at zero pressure only if equations (3) and (4) are omitted. The omission of both of these equations results in disagreement between the quantum yield expression and the data, whereas the inclu-

(8) Some experiments were carried out by one of us (W. A. N., Jr.) in which lead tetramethyl was illuminated by radiation from a zinc spark in the presence of carbon monoxide. A two per cent. acetone solution used as a color filter effectively removed any radiation which would be absorbed by acetone vapor. Leighton and Mortensen [THIS JOURNAL, 58, 448 (1936)] have shown that methyl groups are produced when lead tetramethyl is illuminated. No significant reaction between methyl groups and carbon monoxide could be detected.

(9) Rice and Herzfeld, *ibid.*, 56, 286 (1934).

sion of either one or both makes an agreement possible providing the molecule A_2 is of such a nature that it is always deactivated before dissociating.

We seem forced to one of the following conclusions: (1) fluorescence is emitted; (2) the primarily excited state A_1 changes into another state (or states) without collision, this reaction being necessarily reversible by the principle of microscopic reversibility; (3) the reaction products (especially CO) exert an unexpectedly large effect in deactivating excited acetone molecules; (4) the molecule A_2 , for some reason, is stable or is always deactivated without dissociating.

These possibilities will be discussed in order.

(1) Omitting equation (4) and in the absence of foreign gases the quantum yield becomes

$$\phi = (k_3 + k_6(A))/(k_1 + k_3 + (k_4 + k_5)(A)) \quad (13)$$

If it is assumed that collisions must produce either deactivation or dissociation, $(k_4 + k_5)$ must represent the total number of collisions per excited acetone molecule per second at unit pressure (1 mm.). This number of collisions at 25° is

$$z = 4.78 \times 10^{21} \sigma_1^2 = 1.2 \times 10^7 \quad (14)$$

if σ_1 (the distance between centers at closest approach) is taken as 5×10^{-8} cm.¹⁰ If the quantum yield is 0.65 at zero pressure, the following values of the constants in equation (13) are obtained: $k_1 = 2.56 \times 10^7$; $k_3 = 4.74 \times 10^7$; $k_4 = 0.59 \times 10^7$; $k_5 = 0.61 \times 10^7$. With these values equation (13) fits the quantum yield well within experimental error.

It is now possible to show that 27% of the absorbed quanta should be reemitted as fluorescence at 1 mm. pressure and about 8% at 10 mm. Since the fraction of the radiation reemitted decreases with pressure whereas the amount of radiation absorbed per unit path length increases there will be an optimum pressure for observing the phenomenon. With the incident intensities available the intensity of the fluorescent radiation would not exceed the limit of visibility by a wide margin even if all of the fluorescence occurred in the visible spectrum. A lack of visual observation is not adequate proof of the absence of fluorescence. However, the intensity should be high enough to affect a photographic plate with expo-

(10) The various radii used in this discussion are as follows: acetone 2.5×10^{-8} cm., carbon dioxide 1.83×10^{-8} cm., nitrogen 1.58×10^{-8} cm., ethane 2.0×10^{-8} cm. These are estimated from tables and from interatomic distances and are admittedly very crude values. The results should be taken as verifying one of the general pictures presented to explain the experimental facts rather than as signifying an exact numerical agreement.

ures of thirty to sixty minutes providing the plate is sensitive to the wave lengths reemitted. If fluorescence exists the failure to observe it must be ascribed to this cause, although the plates used should be sensitive to the region from 6000 to 1800 Å.

The question of the existence of fluorescence therefore must be left open.

(2) The introduction of two or more states which may change into each other reversibly without loss of energy makes it possible to derive an equation which will fit the data and still give a quantum yield of unity at zero pressure. The complete evaluation of all of the constants in such an equation is impossible from any experimental data, although conclusions may be drawn with regard to the values of certain ones. The rate of change of A_1 into A_2 and *vice versa* must proceed much more rapidly (at least 100 times) than the spontaneous dissociation of either one and the constant for spontaneous dissociation of the one of longest mean life must be twenty to one hundred times smaller than the number of collisions per second at unit pressure. This means that the mean life must be of the order of 10^{-5} to 10^{-6} sec., although this figure could be reduced somewhat by using a different collision diameter. Obviously any mechanism which will fit the experimental data and still permit the quantum yield to be unity at zero pressure must involve states with long lives.

(3) The reaction products may exert a deactivating effect on excited acetone molecules. However, ethane raises the quantum yield, so that the responsibility would have to be placed on the carbon monoxide. The decomposition was never allowed to proceed very far and the carbon monoxide pressure was usually not greater than 0.01 mm. at the end of an experiment. While fairly good resonance might be expected with carbon monoxide, here again either a long mean life for excited acetone or unreasonably large collision diameters would have to be used to fit the facts.

(4) If the molecule A_2 is stable and does not change back into A_1 , the following equation (similar to (13)) is obtained

$$\phi = (k_3 + k_6(A))/(k_2 + k_3 + k_4(A) + k_5(A)) \quad (15)$$

The numerical values of the constants will be the same as for equation (13) except that k_2 will replace k_1 . The calculated values in Tables III and IV were obtained from equation (15).

From the constants for either equation (13) or equation (15) the mean life of the excited acetone molecule is found to be 1.4×10^{-8} second, which is large enough so that a discrete spectrum should be observed.

The theoretical difficulties involved in introducing a metastable molecule of long life will be considered in the next section. However, since either equation (13) or equation (15) fits the experimental data over the range of observations, they will be used in discussing the effects of added gases.

One observes that the effect of added gases is in each case to cause an increase in the quantum yield. By taking into account the constants already evaluated one finds for the ratio of quantum yield with added gas to that without

$$\phi/\phi_0 = \frac{1 + k_7 P_2 / (k_8(8.13 + P_1))}{1 + (k_6 + k_7)P_2 / (k_4 + k_8)(6.1 + P_1)} \quad (16)$$

where ϕ is the quantum yield at foreign gas pressure of P_2 mm. and acetone pressure of P_1 mm., while ϕ_0 is the quantum yield when $P_2 = 0$. $(k_6 + k_7)$ will be the number of collisions per excited acetone molecule per second at unit pressure of added gas. An examination of the data in Table V reveals the fact that k_6 seems to be small compared to k_7 . If one assumes $k_6 = 0$, the following equations are obtained (radii are given in Ref. 10): for carbon dioxide

$$\phi/\phi_0 = (1 + 1.62P_2 / (8.13 + P_1)) / (1 + 0.79P_2 / (6.1 + P_1)) \quad (17)$$

For nitrogen

$$\phi/\phi_0 = (1 + 1.68P_2 / (8.13 + P_1)) / (1 + 0.82P_2 / (6.1 + P_1)) \quad (18)$$

For ethane

$$\phi/\phi_0 = (1 + 2.00P_2 / (8.13 + P_1)) / (1 + 0.98P_2 / (6.1 + P_1)) \quad (19)$$

Table VII shows the applicability of equations (17), (18) and (19) to the data of Table V.

TABLE VII
COMPARISON OF OBSERVED WITH CALCULATED EFFECTS OF FOREIGN GASES

Acetone pressure, mm.	Foreign gas pressure, mm.	ϕ/ϕ_0 obsd.	ϕ/ϕ_0 calcd.	Foreign gas
1.82	9.8	1.33	1.31	CO ₂
1.81	9.8	1.39	1.31	
1.75	18.4	1.42	1.41	
2.12	2.23	1.13	1.12	N ₂
2.12	3.78	1.33	1.18	
2.34	7.38	1.21	1.30	C ₂ H ₆
2.32	7.18	1.23	1.30	
2.30	12.30	1.31	1.39	

With the exception of one run the agreement between observed and calculated values is satisfactory in the cases of carbon dioxide and nitrogen, thus indicating that practically every collision between an excited acetone molecule and a molecule of these gases leads to dissociation. For ethane the observed values are always lower than the calculated values. Agreement may either be obtained by using 3.4×10^{-8} cm. as the value of σ or by assuming that approximately 10% of the collisions lead to deactivation. In reality the two points of view do not differ materially, since the efficiency factor and the radius cannot be calculated separately. Ethane does possess some bonds similar to those in acetone and hence one should expect a better chance of resonance upon collision than with the other two gases. The fact that ethane is less efficient in producing dissociation than either carbon dioxide or nitrogen agrees with prediction.

III. Theoretical Discussion

As has been shown in the preceding section, many of the aspects of the photochemical decomposition of acetone in the neighborhood of 1900 Å. may be explained on the basis of a simple kinetic picture. The chief difficulty is connected with the fact that the quantum yield, in the apparent absence of fluorescence, does not rise to unity at zero pressure. Several explanations of this fact are possible. There remains the problem of correlating the spectroscopic and photochemical data for the two regions so far investigated.

Mulliken¹¹ has studied the various electronic states of ketones and aldehydes. The symmetry of the acetone molecule may be taken as C_{2v}, the same as formaldehyde, if the rotation of the methyls is considered. The normal state cannot be formed from two methyl groups and carbon monoxide in its ground (¹Σ) state. There are several reasons for believing that this is so: (1) the value of ω_e for normal carbon monoxide¹² is 2167.4 cm.⁻¹ which does not correspond to the frequency of about 1700 cm.⁻¹ observed for all molecules containing the carbonyl group;¹³ (2) the carbon-oxygen distance in carbon monoxide corresponds most nearly to that of a triple bond and the electronic configuration of this molecule may best be described in this way.¹⁴ One would

(11) Mulliken, *J. Chem. Phys.*, **3**, 564 (1935).

(12) Jevons, "Report on Band Spectra of Diatomic Molecules," The Physical Society, London, 1932, p. 286.

(13) See Hibben, *Chem. Rev.*, **18**, 41 (1936).

(14) See Mulliken, *ibid.*, **9**, 373 (1931).

expect a system of two methyl groups and normal carbon monoxide to be repulsive.

The only state of carbon monoxide which has a value of ω_e approximately corresponding to that of the Raman frequency of the carbonyl group is a $^3\Pi$ with a frequency of 1739.3.¹² If this state is split into C_{2v} symmetry by bringing up two methyl groups one can arrive at Mulliken's configuration for the acetone molecule.

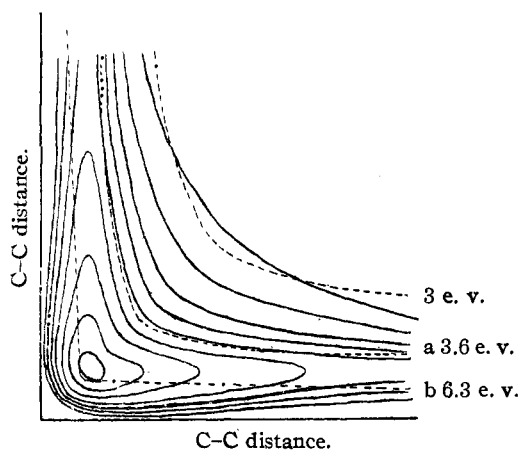


Fig. 1.

Excited states of the acetone molecule must exist which would separate adiabatically into other states of carbon monoxide and normal methyl groups, since the absorption is concerned mainly with electrons in the carbonyl group. Thus there is an excited electronic state of carbon monoxide with $\omega_e = 1182$,¹⁵ which lies 7.13 electron volts above the ground state. Several observers have found upper state frequency differences in aldehyde and ketone absorption corresponding to 1180 to 1200 cm.^{-1} ^{2c} in the absorption region around 3000 Å. In the bands between 1800 and 2000 Å., strong bands separated by 1049 and 1194 cm.^{-1} were found and one of these frequencies is probably a carbon-oxygen frequency. The corresponding state of carbon monoxide is less definite here because no ω_e value is given for the $d^3\Pi$ state.

There are too many degrees of freedom in the acetone molecule to permit a diagram in two dimensions to represent them all. However, one may, for purposes of discussion, hold the energies in the carbonyl group and in the methyl groups constant and furthermore keep the angle between the carbon-carbon bonds constant. With these

(15) Cf. Ref. 12. Henri [*Compt. rend.*, **199**, 849 (1934)] has assigned the states of the carbonyl group in much the same way as that indicated here.

restrictions it is possible to represent the acetone molecule by a contour map after the method of Eyring¹⁶ (Fig. 1). The two carbon-carbon distances are represented by ordinates and abscissas and energy differences are represented by contours. These diagrams may be made only semi-quantitatively since all of the necessary facts for the complete description of the acetone molecule are not known. The stable configuration of acetone will be represented by a point at the bottom of the valley and on the line bisecting the angle between the x and y axes. If Fig. 1 represents the surface for the first excited state of acetone, then the dotted lines may be taken to represent the repulsive state formed from normal $^1\Sigma$ carbon monoxide and two normal methyl groups. Since this state is assumed to be repulsive the surface representing it must be rising fairly steeply and will touch the surface for the upper state (at about 4.1 electron volts) at a point lying on the line bisecting the angle between the x and y axes. From the upper state, therefore, the easiest way of egress would lead to the simultaneous splitting off of two methyl groups as postulated by Norrish.⁵ However, since the "point" of intersection is in reality a "surface" when one considers all degrees of freedom, there should be some chance of splitting off one methyl group alone, although the "pass" over which the molecule would have to go would be somewhat higher than for the other process. It is easily seen that thermal dissociation should occur with the splitting off of one methyl group as postulated by Rice and Herzfeld.⁹ The heat of activation for this process should be the heat of dissociation of the carbon-carbon bond less the energy contained in the various degrees of freedom of the molecule; 70,000 calories is the value chosen by Rice and Herzfeld.⁹

Figure 2 is a vertical cross section cutting across all of the energy levels, keeping both the angle between the carbon-carbon bonds constant and the two carbon-carbon distances equal to each other. This diagram resembles that of a diatomic molecule, but it should be kept in mind that many more degrees of freedom are involved. From spectroscopic information, known heats of dissociation and the photochemical facts one can deduce the vertical distances quite accurately. The manners in which the various curves inter-

(16) Eyring, *Naturwissenschaften*, **18**, 914 (1930); Eyring and Polanyi, *Z. physik. Chem.*, **12B**, 279 (1931).

sect are in agreement with these facts, but the horizontal distances are schematic.

I represents the normal state of acetone and II the upper state for the bands near 3000 Å. Fluorescence should be most strong on the long wave end of this band system. There are two reasons for drawing the upper curve displaced horizontally with respect to the curve of the ground state: (1) the maximum intensity of absorption is displaced toward short wave lengths from the band chosen as the (0,0) band.^{2c} (2) The maximum intensity of fluorescence is in the green. The curves are drawn to account semi-quantitatively for these facts. Dissociation takes place by a transition from II to the repulsive state IV, but there should be some chance of fluorescence in the entire region.

In discussing the near ultraviolet region of the spectrum it must be emphasized that a consistent explanation of the published results is impossible. It has been shown that practically all of the absorbed energy may be accounted for^{4b} by (1) fluorescence, (2) dissociation, (3) deactivation by collision. In order to arrive at this balance it was assumed that the dissociation followed equation (5). However, it has been shown that the quantum yield probably decreases with pressure at 3130 Å.^{4a} A mechanism fitting these facts may be derived by assuming that $k_3 = 0$ and that dissociation of an activated molecule occurs only upon collision. Thus it is seen that the relatively small amount of fluorescence is incompatible with a quantum yield approaching zero at zero pressure. To explain some of the facts in this region Norrish⁵ has introduced the idea of "degradation to heat," which is equivalent to postulating a molecule formed spontaneously from the originally activated molecule, but incapable of dissociation in a time even considerably greater than the time between collisions. It is seen that a difficulty seems to exist in the near ultraviolet similar to that encountered at 1900 Å., but the experimental data, particularly in the former region, are not accurate enough at present so that one is justified in stating whether the difficulties are apparent or real.

Curve III represents the upper state for the spectral region discussed in the present article. Curve IV must lie fairly close to curve III so that there is a fairly high probability of transition to the repulsive state. In general the transition must occur after a period of time longer than that

required for one rotation (between 10^{-10} and 10^{-11} sec.) or the bands would not appear to have sharp edges at low pressures. The mean life of about 10^{-8} second is not in disagreement with this statement. It may be pointed out that the perturbation caused by a collision would be of the right nature to cause a transition to the repulsive level.

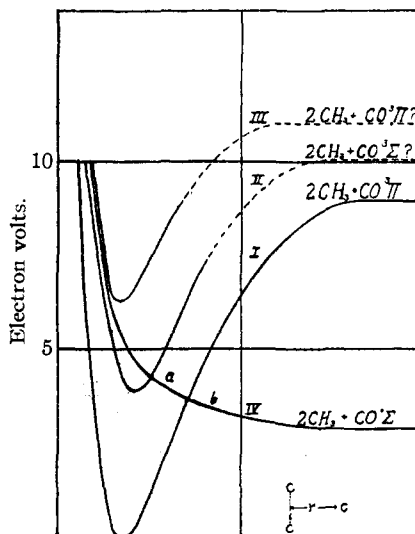


Fig. 2.

Since many of the photochemical facts seem to require the assumption of a state of long life formed spontaneously from the initially excited state, some speculation concerning this matter is in order.

At a first glance one might expect that once a molecule had transferred to the repulsive state IV its lifetime would be less than one period of vibration, about 10^{-13} sec. However, curve IV will not be continuous, but both I and IV will be broken at their intersection, the two upper parts and the two lower parts joining, respectively, to form two new continuous curves.¹⁷ The probability of transition from the upper to the lower of these two new curves may be small enough to increase the mean life of the excited molecules by a large factor. Of course the proper selection rules must be obeyed for a perturbation of this type to occur. Whether or not the mean life would be long enough to account for the photochemical results is an open question, although so many different configurations may be assumed by the molecule that this is not impossible.

Once the molecule is on curve I there will be the

(17) Cf. Eyring and Stearn, *J. Chem. Phys.*, **3**, 778 (1935).

possibility of dissociation into CH_3CO and CH_3 . Damon and Daniels^{4a} do note a decrease in quantum yield at high intensities. Most of the known facts for the 3000 Å. region may be explained by assuming a recombination reaction between CH_3CO and CH_3 which takes place largely on the walls but partially in the gas phase. Thus the yield may be made to approach zero at zero pressure even though the fluorescence is small. Dissociation would follow collision, supporting the increase in yield with pressure,^{4a} and might be partially into 2 CH_3 and CO and partially into CH_3CO and CH_3 . The chief arguments against this explanation are: (1) the supposed instability of the CH_3CO radical;⁹ (2) the fact that the photochemical formation of diketones has not been observed.

Any CH_3CO radical produced by the dissociation of a molecule excited in the 1900 Å. region would possess so much energy that it should spontaneously dissociate. It seems very unlikely, therefore, that a recombination reaction can be responsible for the low yield in this part of the spectrum.

At least one other repulsive surface must exist, namely, that between normal carbon monoxide and normal ethane. However, ethane can be produced in one step only if the angle between the carbon-carbon bonds is varied and hence this surface cannot be represented on the diagrams. Moreover, there will be steric effects which will prevent transitions to this state from being very probable.

Certain relationships to the pictures for formaldehyde, acetaldehyde and methyl ethyl ketone may be stated. In formaldehyde there will be no steric effect to prevent transition to the repulsive surface formed by normal hydrogen and normal carbon monoxide and the observed quantum yield is unity.¹⁸ A molecule with sufficient energy

might dissociate in other ways. The methane-carbon monoxide surface must be important in acetaldehyde, since the steric effect would be considerably less than in acetone.¹⁹ However, some decomposition in this case must be by way of the methyl-carbon monoxide-hydrogen atom surface since free radicals have been detected to some extent in this case. In methyl ethyl ketone several other repulsive surfaces must intervene and several products are observed upon illumination.

In conclusion the authors wish to express their appreciation to the Chemistry Department of the Johns Hopkins University for the loan of the rotating spark gap.

Summary

1. The quantum yield of acetone decomposition with approximately monochromatic radiation from the aluminum spark about 1900 Å. has been investigated. It is (a) independent of intensity over quite wide limits; (b) dependent upon acetone pressure, increasing at low pressures, the limiting value appearing to be about 0.65; (c) increases with the addition of nitrogen and carbon dioxide and to a lesser extent with the addition of ethane; (d) is apparently increased by the action of excited mercury unless precautions are taken to avoid this error.

2. No fluorescence could be detected.

3. Some difficulty is encountered in explaining the low quantum yield at low pressures, but otherwise the facts fit a simple kinetic picture.

4. The photochemical decomposition of acetone near 3000 Å., the decomposition near 1900 Å. and the various facts of spectroscopy and fluorescence may mostly be correlated with the use of potential energy surfaces.

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(18) Norrish and Kirkbride, *J. Chem. Soc.*, 1518 (1932).

(19) See Norrish, *Trans. Faraday Soc.*, **30**, 107 (1934).