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W. Albert Noyes Jr. and Leon M. Dorfman

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Photo-Chemical Studies. XL. The Mechanism of the Photo-Chemical **Decomposition of Acetone**¹

W. Albert Noyes, Jr. and Leon M. Dorfman Department of Chemistry, University of Rochester, Rochester, New York (Received April 16, 1948)

The data now available indicate quite strongly that the photo-chemical decomposition of acetone proceeds mainly if not entirely by a free radical mechanism. The various steps are reviewed and the evidence for them given. At high pressures where wall effects may be neglected certain definite conclusions are possible. In the region where some reactions are both homogeneous and heterogeneous the proof for all steps is not available and would be difficult to obtain. The analyses for some of the known products are not satisfactory for the small amounts formed. Nevertheless, it is believed that the steps proposed are adequately substantiated, and that the difficulties of obtaining further information are so great as probably not to warrant more effort along certain lines.

`HE first quantitative experiments on the photo-chemical decomposition of acetone vapor seem to have been performed by Porter and Iddings,² but the first work studying the effects of many variables is due to Damon and Daniels.³ Since this early work many articles have been published. The data are often in apparent conflict, and the present article is being written to present a consistent mechanism for the photo-chemical decomposition of acetone and to show that most of the undisputed facts are in accord with this mechanism. Certain points have not been proved beyond a reasonable doubt because of experimental difficulties, but strong support for their validity is found from many sources.

The present article does not contain a complete bibliography of the photo-chemical decomposition of acetone. Such a review article covering work through 1946 has been published recently by Davis,⁴ and frequent reference will be made to it.

THE PRIMARY PROCESS (PRELIMINARY)

Three different primary dissociation processes for the photo-chemical decomposition of acetone vapor have been proposed:

CH₃COCH₃+
$$h\nu$$
 = C₂H₆+CO, (1)⁵⁻⁷
CH₃COCH₃+ $h\nu$ = CH₃+COCH₃, (2)⁷⁻⁹

followed by

$$a \operatorname{COCH}_3 = a \operatorname{CO} + a \operatorname{CH}_3$$
 (3)⁸

(where a is the fraction of the initially formed COCH₃ radicals which retain enough energy following (2) to dissociate immediately and (1-a)is the fraction which attain thermal equilibrium with the surroundings and whose reactions follow a pattern dependent on temperature and other experimental conditions)

$$CH_{3}COCH_{3} + h\nu = 2 CH_{3} + CO.$$
(4)⁷

In addition to the preceding reactions, another primary process must be included

$$CH_{3}COCH_{3} + h\nu = CH_{3}COCH_{3}'.$$
 (5)

Reaction (5) is necessary because acetone exhibits a weak blue fluorescence¹⁰ which possesses some discrete structure.11

Recent work¹² indicates that ethane is formed

⁵ R. Spence and W. Wild, J. Chem. Soc. 352 (1937);

- ⁶ M. H. Feldman, M. Burton, J. E. Ricci, and T. W. Davis, J. Chem. Phys. 13, 440 (1945).
 ⁷ F. W. Kirkbride and R. G. W. Norrish, Trans. Faraday
- Soc. 27, 404 (1931)
- ⁸ D. S. Herr and W. A. Noyes, Jr., J. Am. Chem. Soc. 62, 2052 (1940). ⁹ M. S. Matheson and W. A. Noyes, Jr., J. Am. Chem.

16, 557 (1948).

¹ This work was supported by Contract N6onr-241, Task I, with the Office of Naval Research, United States

<sup>Navy.
² C. W. Porter and C. Iddings, J. Am. Chem. Soc. 48, 40 (1926).
³ G. H. Damon and F. Daniels, J. Am. Chem. Soc. 55, 2663 (1933).
⁴ W. Davis Ir. Chem. Rev. 40, 201 (1947).</sup>

⁴ W. Davis, Jr., Chem. Rev. 40, 201 (1947).

Soc. 60, 1857 (1938). ¹⁰ See R. E. Hunt and W. A. Noyes, Jr., J. Am. Chem. Soc. 70, 467 (1948) for a description of fluorescence and

<sup>for a bibliography of the subject.
¹¹ G. W. Luckey, A. B. F. Duncan, and W. A. Noyes, Jr., J. Chem. Phys. 16, 407 (1948).
¹² L. M. Dorfman and W. A. Noyes, Jr., J. Chem. Phys.</sup>

mainly, if not solely, by reaction between methyl radicals. Under conditions of low light intensity and relatively high pressure the amount of CH4 may exceed the amount of C₂H₆ very considerably. These facts do not exclude reaction (1)completely, but indicate that it is of minor importance compared to dissociation into radicals. It is unnecessary to assume that (1) occurs during the fluorescence act.¹¹ For these and other reasons to be given later reaction (1) is neglected in the following discussion.

It will be necessary to state very clearly the meaning of the primary quantum yield (ϕ) . Every molecule which absorbs a quantum must undergo either one or the other of reactions (1), (2), (4), or (5). Reaction (4) would be difficult to distinguish from (2) followed by (3). This point will be discussed later. The following facts are pertinent: (a) At temperatures below 100°C biacetyl is known to be one of the products;⁵ (b) at temperatures above 100°C very close to one molecule of carbon monoxide is formed per absorbed quantum;8 (c) under otherwise comparable experimental conditions the yield of carbon monoxide at 25°C is greater at 2537A than it is at 3130A;⁸ (d) at temperatures of 60°C and above, the photo-chemical decomposition of acetone at 2537A in the presence of iodine vapor indicates a primary yield very close to unity;¹³ (e) at 80° and 90°C at 3130A in the presence of iodine vapor the yield of CH₃I is about 0.85 molecule per quantum.¹⁴

Fact (a) can best be explained by assuming some formation of CH₃CO in the primary process. Hence a part of the primary process at least must follow (2).

Fact (c) makes it necessary to assume that ais dependent on wave-length and facts (a), (b), and (c) make it necessary to assume that a and perhaps also ϕ are dependent on temperature. Temperature dependence for ϕ is also strongly indicated by the decrease in fluorescence efficiency with increase in temperature when 3130A is the exciting radiation.¹⁰

Fact (d) indicates that ϕ at 2537A is probably close to unity at all temperatures. No supporting fluorescence data are available at this wavelength. Fact (e) does not lead to positive conclusions, although it tends to support the statement that ϕ is less than unity at 3130A at 80°C. This is particularly true since some CH₃I would doubtless be formed from CH₃ radicals resulting from the dissociation of CH₃CO. The yield of CH₃COI was always considerably below the vield of CH₃I.

The fate of the excited molecules produced by (5) at 3130A (tentatively it can be assumed that none is formed at 2537A) is uncertain. They may do one of the following: (a) fluoresce; (b) be transferred to another electronic state by collision; 5,10 (c) be deactivated by collision; (d) "predissociate by collision." The absolute fluorescence efficiency is not known but is probably below 0.05 at moderate pressures.³ Transfer to another electronic state, probably through the agency of collisions, is strongly indicated by the fluorescence data¹⁰ and by the long lifetimes of the molecules responsible for fluorescence.¹⁵ The validity of the latter point as applied to fluorescence in the gas phase has not been established since the data were obtained for solid acetone.

The distinction between (c) and (d) cannot be obtained from fluorescence data since either process leads to fluorescence quenching. It is at this point that the greatest ambiguity arises both in defining the primary quantum yield and in determining the magnitude of the primary yield.

It is concluded from the above discussion that process (1) occurs to such a minor extent as to be unimportant, that process (4) satisfactorily represents the facts at temperatures above 100°C, and that the following must be included in the reaction mechanism at temperatures below $100^{\circ}C: (2), (3), (5)$. It is further necessary to conclude that a is dependent on wave-length.

It is now necessary to define the primary quantum yield in terms of Eqs. (2), (3), and (5), assuming that (5) may be followed in some instances by (2) and perhaps (3). It seems best to do this in terms of rate of formation of methyl radicals. As will be shown later, there are no reactions, either primary or secondary, other than (2), (3), and the thermal decomposition of CH₃CO radicals, which lead to the formation of CH_3 radicals. Similarly, reaction (3) and the

¹⁸ S. W. Benson and G. S. Forbes, J. Am. Chem. Soc. 65, 1398 (1943); cf. reference 4. ¹⁴ E. Gorin, J. Chem. Phys. 7, 256 (1939).

¹⁵ W. E. Kaskan and A. B. F. Duncan, J. Chem. Phys. 16, 223 (1948).

thermal decomposition of CH₃CO radicals seem to be the only ones which lead to CO formation. This neglects reaction (4) at low temperatures (see below). It makes no difference whether there is a delay of a fraction of a second following absorption and before dissociation except that such a delay might make ϕ pressure dependent.

It is possible to write

$$CH_{3}COCH_{3}+h\nu=CH_{3}+COCH_{3};$$

$$(+d(CH_{3})/dt)_{1}=\phi I_{a}.$$
 (6)

(Reaction (6) is taken to represent all molecules which dissociate immediately or eventually to give CH₃+COCH₃.)

$$COCH_{3} = CO + CH_{3}; (+d(CH_{3})/dt)_{2} = a\phi I_{a} = (+d(CO)/dt)_{1},$$
(7)

$$COCH_{3} = CO + CH_{3}; (+d(CH_{3})/dt)_{3} = k_{1}(COCH_{3}) = (+d(CO)/dt)_{2}.$$
 (8)

It could be considered that the fraction $a\phi$ of the absorbing molecules follows reaction (4), thus leading to the same rate equations. Equation (8) represents the thermal decomposition of COCH₃ radicals which have come to thermal equilibrium with the surroundings. It is evident that if $T < 100^{\circ}$ C.

$$+d(CH_3)/dt \cdot (1/I_a) = \phi + a\phi +k_1(COCH_3)/I_a, \quad (9) +d(CO)/dt \cdot (1/I_a) = a\phi$$

$$-k_1(\text{COCH}_3)/I_a = \Phi_{\text{CO}}, \quad (10)$$

$$+d(\mathrm{CH}_3)/dt \cdot (1/I_a) - \Phi_{\mathrm{CO}} = \phi.$$
(11)

Under some conditions $+d(CH_3)/dt$ can be determined from the quantum yields of the products, thus permitting an evaluation of ϕ . The value so obtained is subject to considerable error because of the way in which the data must be treated. At low temperatures, however, the recombination of CH₃ and COCH₃ to form $CH_{3}COCH_{3}$ makes the determination of ϕ subject to even greater uncertainties. These matters will be treated further after consideration has been given to the secondary reactions.

SECONDARY REACTIONS

The secondary reactions during photo-chemical acetone decomposition may be obtained by a consideration of the reactions of CH₃ and COCH₃ radicals. There seem to be no secondary reactions involving CO at the temperatures used in most of the experimental work.

The following compounds are known to be produced during the reaction: CH_4 , C_2H_6 , CO, $(CH_{3}CO)_{2}(B)$,⁵ $CH_{3}COCH_{2}CH_{3}(E)$.¹⁶ The first three are the ones for which analyses are practicable in most of the work. An additional compound $(CH_2COCH_3)_2(D)$, is certainly formed whenever the CH₄ yield is high. It has been identified among the products of the thermal reaction of CH₃ radicals with acetone,¹⁷ but it has never been possible to identify it positively in the small quantities in which it is produced during the photo-chemical reaction. One other compound is theoretically possible at low temperatures: CH₃COCH₂COCH₃. However, the amount of this compound should be small at room temperature, and it should not be formed at all at temperatures over 100°C where the COCH₃ radical is quite unstable. Still other products identified at high temperatures¹⁶ need not be considered here.

Two points need special emphasis before starting a discussion of secondary reactions. Some of the reactions involve combinations of radicals and hence depend on the second power of radical concentrations at pressures such that diffusion to the walls is unimportant. If the various radical reactions are sufficiently rapid so that the radicals to a good approximation may be considered not to diffuse out of the light beam, quantitative conclusions are possible provided the shape of the light beam is known. However, the calculations prove to be extremely difficult if the beam is not parallel. Moreover, even with a parallel beam the number of quanta absorbed per unit volume per second will progressively decrease with increase in distance from the window through which the light is incident on the cell. While it is theoretically possible to derive an exact expression when I_a varies in this manner,18 the labor is very great, and the results are not accurate unless the radical recombination

¹⁶ A. O. Allen, J. Am. Chem. Soc. 63, 708 (1941). Methyl ethyl ketone was identified by Allen at temperatures of 250-350 °C. It should be formed whenever CH₄ is produced in appreciable quantities, but a quantitative analysis for it in the presence of a large amount of acetone is very difficult.

¹⁷ F. O. Rice, E. L. Rodowskas, and W. R. Lewis, J. Am. Chem. Soc. **56**, 2497 (1934). ¹⁸ Cf. W. A. Noyes, Jr., Cold Spring Harbor Symposium in Quant. Biol. **3**, 37 (1935).

reactions are very fast. In most of the work on acetone the percentage absorption is sufficiently low to permit use of a mean value of I_a in the light beam to a good first approximation.

These considerations make a quantitative treatment of much of the photo-chemical work on acetone impossible. It has been necessary to base most of the quantitative tests of the mechanism on data obtained with parallel or nearly parallel light beams with sufficiently accurate intensity measurements to permit a calculation of mean I_a . The latter is expressed in quanta absorbed per cm³ per second.

Only qualitative conclusions are possible in

 $2 \text{ COCH}_3 = (\text{COCH}_3)_2$ $2 \text{ CH}_3 = \text{C}_2\text{H}_6$

 $CH_3 + COCH_3 = CH_3COCH_3$

TABLE I. Quantum yields at 122°C.*

Run No.	9	4 <i>b</i>	4 a	11	12
PC2He (fnd.)	03.0	0.27	0.25	0,17	0,17
PC2Hs (calc.)	0.67	0.34	0.34	0.19	0.19
PCH4 (fnd.)	0.41	1.06	1.21	1.11	1.32
PCO (assumed)	1.0	1.0	1.0	1.0	1,0
×10 ⁻¹²)	2.86	0.203	0.201	0.0875	0.0743
P (mm)	117.4	107.2	107.4	123.2	115.1

* See reference 12.

the intermediate pressure region (roughly 10 mm to 50 mm) where homogeneous reactions between radicals and diffusion of radicals to the walls are both important. At very low pressures data are scarce.

Reactions (6)-(8) will be followed by

;
$$k_2(\text{COCH}_3)^2$$
 (12)

;
$$k_3(CH_3)^2$$
 (13)

;
$$k_4(CH_3)(COCH_3)$$
 (14)

$$CH_3 + CH_3COCH_3 = CH_4 + CH_3COCH_2 ; k_5(CH_3)(A)$$
(15)

$$2 \operatorname{CH}_{2}\operatorname{COCH}_{3} = (\operatorname{CH}_{2}\operatorname{COCH}_{3})_{2} \qquad ; k_{6}(\operatorname{CH}_{2}\operatorname{COCH}_{3})^{2} \qquad (16)$$

$$CH_3 + CH_2COCH_3 = CH_3COCH_2CH_3 \quad ; k_7(CH_3)(CH_2COCH_3)$$
(17)

$$CH_{3}CO + CH_{2}COCH_{3} = CH_{3}COCH_{2}COCH_{3}; k_{3}(CH_{3}CO)(CH_{2}COCH_{3}).$$
(18)

(A) =concentration of acetone.

Certain relationships are now evident by imposing the conditions for material balance:

$$N_{\rm CH_3} = 2 N_{\rm C_2H_6} + N_{\rm CH_4} + N_E + N_A', \quad (19)$$

where $N_{\text{CH}_3} = \text{number of CH}_3$ radicals produced, $N_{\text{C}_2\text{H}_6} = \text{number of ethane molecules formed}$, $N_{\text{CH}_4} = \text{number of methane molecules formed}$, $N_E = \text{number of molecules of methyl ethyl ketone}$ formed, $N_A' = \text{number of molecules of acetone}$ reformed.

$$2 N_{\rm CO} + 2 N_B + N_{AA} = N_{\rm CH_3} - N_A' = 2 N_{\rm C_2H_6} + N_{\rm CH_4} + N_E, \quad (20)$$

where N_B = number of molecules of biacetyl produced, N_{AA} = number of molecules of acetyl acetone produced.

$$N_{\rm CH_4} = N_E + 2 N_D + N_{AA}, \tag{21}$$

where N_D = number of molecules of $(CH_2COCH_3)_2$ produced.

At low temperatures CH_4 , C_2H_6 , CO, $(CH_3CO)_2$, $CH_3COCH_2CH_3$, $(CH_2COCH_3)_2$, and $CH_3COCH_2COCH_3$ can all be formed, and in

addition some of the radicals can recombine to form acetone. If the first three are determined experimentally, five unknowns remain with only three equations relating them. Indeed, in the absence of a knowledge of ϕ , N_{CH_3} must also be considered as an unknown. Consequently, a gas analysis for the easily determinable gases will not serve to permit even an indirect calculation of the yields of all of the products.

Certain experimental conditions may be chosen which do make a quantitative treatment of the system possible provided accurate values of N_{CH_4} , $N_{C_2H_6}$, and N_{CO} are available.

Condition 1

Light intensity sufficiently high to make NCH₄ negligible compared to NC_2H_6 : If $NCH_4=0$, $N_E = N_D = N_{AA} = 0$. Hence,

$$N_B = N_{C_2H_6} - N_{CO},$$
 (22)

$$N_{\rm CH_3} = 2 N_{\rm C_2H_6} + N_A'. \tag{23}$$

Values of N_B calculated from Eq. (22) will not be very accurate unless $N_{C_2H_6}$ and N_{CO} are known with very high accuracy.

Condition 2

Temperatures over 100°C: Under these conditions the COCH₃ radical is sufficiently unstable to reduce the rate of formation of $(COCH_3)_2$ to a negligible value. Hence,

$$N_D = N_{\rm C_2H_6} + N_{\rm CH_4} - N_{\rm CO}, \tag{24}$$

$$N_E = 2 N_{\rm CO} - 2 N_{\rm C_2H_6} - N_{\rm CH_4}.$$
 (25)

 N_D and N_E calculated in this way will be subject to considerable error.

In the following discussion the quantum yield Φ_X of the species X is defined by the expression

$$d(X)/dt \cdot (1/I_a) = \Phi_X, \qquad (26)$$

where d(X)/dt is the local rate of formation (or disappearance) of X in the light beam, and I_a is the number of quanta absorbed per cubic centimeter per second in the light beam. It should be noted particularly that the differential is an absolute and not a net rate. Actually, this is not the experimentally determined quantum yield which is

$$N_X/V_L \int_0^t I_a dt = \Phi_X', \qquad (27)$$

where N_X represents the total number of molecules of X formed (or disappeared) in the entire reaction system and V_L is the volume of the light beam. I_a in (27) is the mean number of quanta absorbed per cubic centimeter per second in the light beam. For a rigorous treatment



FIG. 1. The quantum yields of methane (\bigcirc) and of ethane (\bigcirc) as a function of $I_a/(A)^2$. The curves are the theoretical ones from Eqs. (33) and (34). The theoretical yields for ethyl methyl ketone (*E*) and for biacetonyl (*D*) as obtained from calculated values of the yields of methane and of ethane by means of Eqs. (24) and (25) are also shown. Each of the two points for $\Phi c_2 H_6$ near the origin represents two results.

 $V_L \int_0^t I_a dt$ should be replaced by an integral $\int_0^t \int_0^{V_L} I_a dV dt$. This integral can only be obtained if I_a is known as a function of V.

One is justified in placing

$$d(X)/dt \cdot (1/I_a) = \Phi_X = N_X/V_L \int_0^1 I_a dt \quad (28)$$

if the species X for which the quantum yield is being determined does not itself undergo further reaction. Thus if the compound (CH₂COCH₃)₂ reacts with CH₃ radicals (which it certainly would if its concentration became high) Eq. (27) could be used to calculate the net quantum yield of its formation. However, $(CH_2COCH_3)_2$ is a stable compound and will immediately begin to diffuse out of the light beam as soon as it is formed. Consequently, its concentration in the light beam cannot be calculated in any simple manner as would be possible for short-lived free radicals. This question is unimportant except when it would be desired to use steady-state equations for some of the products which might undergo further reaction. Thus biacetyl is known not to build up to a very high concentration,¹⁹ probably because it reacts either with free radicals or, with excited acetone molecules, and its rate of formation could be equated to its rate of disappearance after long exposures. However, this could only be done in deriving a rate equation if due account is taken of the fact that (barring thermal reactions) the formation and the disappearance occur mainly in the light beam.

For the reasons just given a quantitative treatment of the photo-chemical decomposition of acetone must be based on studies during which the percentage decomposition is very small, i.e., during the early stages of the reaction and long before the rates of disappearance of products become appreciable. The theoretical treatment of a situation in which the products are allowed to accumulate is almost impossible unless the light beam fills the entire vessel, and there is no dead volume such as a McLeod gauge. These restrictions reduce even further the data which can be considered for a quantitative test of the reaction mechanism.

 $^{^{19}}$ G. M. Almy and S. Anderson, J. Chem. Phys. 8, 805 (1940).

TEST OF THE MECHANISM AT TEMPERATURES OVER 100°C

It is wise to subject the proposed mechanism to as many tests of validity as possible. One of these has already been published¹² and may be stated as follows (by reference to Eqs. (13) and (15)):

$$\Phi_{\rm C_2H_6^{\frac{1}{2}}}/\Phi_{\rm CH_4} = (k_3I_a)^{\frac{1}{2}}/k_5(A), \qquad (29)$$

where (A) is the concentration (or pressure) of acetone. This equation has been found to be obeyed within experimental error both at 25°C and at 122°C, thus furnishing evidence that ethane and methane are formed by the reactions indicated.

Another relationship (from Eqs. (13), (16), and (17)) would be

$$\Phi_{\rm C_2H_6}\Phi_D/\Phi_{E^2} = k_3 k_6/k_7^2. \tag{30}$$

 Φ_D and $\Phi_E(T>100^{\circ}\text{C})$ in this equation may be obtained indirectly from Eqs. (20) and (21), since $N_B = N_{AA} = 0$. Making the proper substitutions gives the following result:

$$\frac{\Phi_{C_{2}H_{6}}(\Phi_{C_{2}H_{6}} + \Phi_{CH_{4}} - \Phi_{CO})}{(2\Phi_{CO} - 2\Phi_{C_{2}H_{6}} - \Phi_{CH_{4}})^{2}} = k_{3}k_{6}/k_{7}^{2} = \text{const.} \quad (31)$$

Any errors in individual quantum yields will be badly magnified in ascertaining whether a true constant is obtained from Eq. (31). This equation is valid only at temperatures such that the yield of biacetyl is negligible, whereas Eq. (29) is valid at any temperature. Of course, Eq. (30) should be valid at any temperature, but the necessary yields for determining its validity are not available.

Only one series of runs¹² is available for testing Eq. (31). The constant varies from 0.5 to 1.6, but the nature of Eq. (31) is such that good constancy could scarcely be expected. Thus an error of 0.01 in determining the fraction of C_2H_6 in the reaction products will cause an error of at least 0.03 in $\Phi_{C_2H_6}$. With the small amounts of gas obtained at low intensities, duplicate runs frequently differ by as much as 0.03 in the fraction of C_2H_6 and other gases.

As will be shown in later paragraphs, there is another way of evaluating k_3k_6/k_7^2 from quantum yields of methane alone. Neither method can

TABLE II. The calculation of k_3k_6/k_7^2 at 122°C.

Run No. and ref.	Temp. °C	Press mm	(A) Molecules per cm ³	Ia Quanta/ cm ³ /sec.	ФСН₄	k3k6/k7 ² (dimen- sion- less)
6A19	126	194	4.69×1018	16.4×1012	0.40	1.2
9 ¹²	122	117	2.87	2.86	0.41	
$7A^{19}$	120	205	5.01	2.20	0.91	3.9
8A ¹⁹	120	233	5.72	2.30	0.97	
9A ¹⁹	127	152	3.67	2.40	0.60	7.1
$10A^{19}$	122	95.	2.32	2.70	0.62	0.5
$11A^{19}$	126.5	109	2.63	2.10	0.63	1.0
$4b^{12}$	121.2	107	2.62	0.203	1.06	1.6
$4a^{12}$	122	107	2.62	0.201	1.21	
1112	123	123	3.00	0.0875	1.11	0.1
1212	123	115	2.81	0.0743	1.32	0.7
					Mean	2.0

claim high accuracy, although the equations of the theory undoubtedly give the correct trend to the results. In order to show the difficulty of applying Eq. (31) and to show that, in general, it gives results within experimental error of the found values, some comparisons are made in Table I. The calculated values are based on $k_3k_6/k_T^2 = 2.0$ (see Table II).

In Table I $\Phi_{C_2H_6}$ is calculated by assuming Φ_{CH_4} , as taken from the smooth curve in Fig. 1, to be correct. Any more precise test of the mechanism would involve obtaining data of greater precision than has hitherto been possible.

A complete expression relating Φ_{CH_4} to intensity and acetone pressure is

$$0 = K_{a}^{2}(4K_{b}-1) \left\{ \frac{(\Phi_{CH_{4}}I_{a}/(A))^{2}}{I_{a}(2-\Phi_{CH_{4}})} \right\}^{2} + K_{a} \left\{ \frac{1-\Phi_{CH_{4}}}{2-\Phi_{CH_{4}}} - 4K_{b} \right\} \times \left\{ \frac{(\Phi_{CH_{4}}I_{a}/(A))^{2}}{I_{a}(2-\Phi_{CH_{4}})} \right\} + K_{b}, \quad (32)$$

where $K_a = k_3/k_5^2$, $K_b = k_3k_6/k_7^2$.

 K_a at 122°C has been obtained¹² from a straight line plot of $\Phi_{CH_4}/\Phi_{C_2H_6^{\frac{1}{2}}} vs. (A)/I_a^{\frac{1}{2}}$ and has the value 9.8×10^{24} molecules sec. cm⁻³. It is now possible to solve for K_b from quantum yields of CH₄ under various experimental conditions. Some of the data were reported previously,¹² and some have been obtained by Davis.^{19a}

Table II shows the results of the calculations. Runs 9 and 8A gave negative values, and Run 4a gave an extremely high value.

¹⁹⁸ W. Davis, Jr., J. Am. Chem. Soc. 70, 1867 (1948).

It should be noted that the data in Table II cover a more than 200-fold change in intensity. In view of the sensitivity of K_b to values of Φ_{CH_4} and I_a , the constancy of K_b is as good as can be expected. As can be seen from Fig. 1, probably the values of K_a and K_b may not be the best ones for fitting the data, but the accuracy is such as not to warrant a more extended treatment. The use of $(1-\Phi_{CH_4})$ and of $\Phi_{CH_4}^4$ amplifies errors considerably.

Since K_a and K_b have been determined, it is now possible to calculate Φ_{CH_4} as a function of $I_a/(A)^2$. If I_a is expressed in quanta per cm³ per second and (A) is in molecules per cm³, the resulting equation for $T=122^{\circ}$ C is

$$672.3\Phi CH_4^4 x^2 + 68.6\Phi CH_4^3 x + \Phi CH_4^2 (2 - 147x) - 8\Phi CH_4 + 8 = 0, \quad (33)$$

where $x = (I_a/(A)^2) \times 10^{24}$. Figure 1 shows the experimental points and the theoretical curve taken from Eq. (33). It is evident that the equation gives the correct trend to the results and reproduces them within experimental error.

It is also possible to establish an equation for ΦC_{2H_6} in terms of $(A)/I_a^{\frac{1}{2}}$

$$7\Phi_{C_{2}H_{6}^{2}}+2.24\Phi_{C_{2}H_{6}^{\frac{3}{2}}}y+\Phi_{C_{2}H_{6}}(0.204y^{2}-15) -\Phi_{C_{2}H_{6}^{\frac{1}{2}}}2.56y+8=0, \quad (34)$$

where $y = ((A)/I_a^{\frac{1}{2}}) \times 10^{-12}$. Figure 1 shows the theoretical curve and the experimental points for $\Phi_{C_2H_6}$ as a function of $I_a/(A)^2$. The experimental points are not very numerous in this instance.

Thus the mechanism embodied in Eqs. (6)-(8) and (12)-(18) accounts for the yields of CO, CH₄, and C₂H₆ within experimental error. It should be noted particularly, however, that data must be carefully obtained or the resulting equations cannot be employed. Thus I_a expressed in quanta absorbed per cubic centimeter per second is critical, and a diverging or converging light beam will make exact calculations impossible.

A few words may be said concerning the primary process at temperatures over 100°C. All authors agree that Φ_{CO} under these conditions is approximately 1 and varies little if at all with temperature.²⁰ This could be explained in one of

the following ways: (a) Reaction (4) with one molecule of CO and two CH₃ radicals being formed per quantum absorbed; (b) reactions (6) and (7) with ϕ and a both unity; (c) reactions (6)-(8) with $\phi = 1$, a < 1, and k_1 sufficiently large to make the decomposition of the COCH₃ radical very rapid compared to other reactions it might undergo. No definite way of deciding between these possibilities is available. However, the data of Gorin¹⁴ show guite definitely that some COCH₃ radicals are produced in the primary process at temperatures of 80-90°C. The energy of activation for reaction (8) is not known precisely but has been estimated at from 10 to 18 kcal.⁴ Thus (8) will have a very high temperature coefficient and would be expected to be very rapid at temperatures over 100°C. This could mean merely that the COCH₃ radicals formed by (6) would be less apt to lose energy at high temperatures than at low. The data are in agreement with possibility (b) above, but (c) cannot be excluded.

The equivalent of reaction (15) may occur in mixtures of acetone and other organic molecules. Thus Leermakers²⁰ has shown that considerable quantities of CH_4 are produced in mixtures of acetone and dimethyl ether. This fact adds further support to the mechanism.

A word about the low pressure case with diffusion of radicals to the walls as the predominating process may be said. The unknown here is the possible reaction of methyl radicals with acetone adsorbed on the walls. The meager data on this point²⁰ tend to the belief that at 403°C the amount of ethane produced even at a pressure of 12.6 mm is negligible but that the C_2H_6/CH_4 ratio increases with decreasing temperature. At 122°C it seems probable that a large fraction of the CH₃ radicals which diffuse to the walls forms C_2H_6 rather than CH₄, but more data are needed on this point.

TEST OF THE MECHANISM AT TEMPERATURES NEAR 25°C

Reference to Eqs. (19)-(21) shows that there are too many unknowns to be calculated from analyses for CO, C_2H_6 , and CH_4 . However, it is possible to choose experimental conditions such that $\Phi_{CH_4} \ll \Phi_{C_2H_6}$. When methane is formed, it has been shown that the same type of mechanism

²⁰ See reference 4 for a summary. References 19 and 8 have data on this point, but the data of J. A. Leermakers, J. Am. Chem. Soc. 56, 1900 (1934) are most significant since they cover the temperature range 163-405 °C.

(36)

holds for CH₄ and for C₂H₆ formation at 25°C as at 122°C.¹² Thus reactions (15) and (13) seem to be correct at both temperatures. Indeed the data are more extensive at 25°C and prove the validity of these two equations particularly well at that temperature.

From Eqs. (12) and (22) it is seen that

$$\Phi_B = k_2 (\text{COCH}_3)^2 / I_a = \Phi_{\text{C}_2\text{H}_6} - \Phi_{\text{C}_0}, \quad (35)$$

when Φ_{CH_4} is negligible. Similarly, from Eqs. (7) and (8)

$$\Phi_{\rm CO} = k_1 ({\rm COCH}_3) / I_a + a\phi.$$

$$(\Phi_{\rm CO} - a\phi)/(\Phi_{\rm C_2H_6} - \Phi_{\rm CO})^{\frac{1}{2}} = k_1 I_a^{\frac{1}{2}}/k_2^{\frac{1}{2}}.$$
 (37)

It should be noted that k_1 and k_2 should be independent of wave-length, whereas *a* probably depends on wave-length since the residual energy left in the COCH₃ radical will depend on the energy taken up by the absorbing molecules.

The following data are taken from earlier work:⁸

	$\Phi\mathrm{C_{2H_{6}}}$	Фсо	I_a
3130A	0.19	0.11	10
2537	0.36	0.28	10

(P = 100 mm, $T = 25^{\circ}\text{C}$, I_a is in arbitrary units, where 1 unit is approximately 2×10^{12} quanta per cm³ per second.)

Substituting the appropriate values in Eq. (37) and equating for the two different wave-lengths gives

$$0.17 = (a\phi)_{2537} - (a\phi)_{3130}.$$
 (38)

Of course it is impossible to get individual values by this method. The previous value⁸ for the difference in Eq. (38) obtained by making certain assumptions with regard to the constants was 0.15.

An examination of the proposed mechanism shows that there are only two reactions which lead to the disappearance of acetone molecules: (6) and (15). There is also one reaction which leads to reformation of acetone molecules: (14). With these facts in mind it is seen that

$$\frac{k_4^2 (\text{CH}_3)^2 (\text{COCH}_3)^2}{k_2 (\text{COCH}_3)^2 k_3 (\text{CH}_3)^2} = \frac{k_4^2}{k_2 k_3}$$
$$= \frac{(\phi + \Phi_{\text{CH}_4} - \Phi_A)^2}{\Phi_{\text{C}_2\text{H}_6} \Phi_B}, \quad (39)$$

where Φ_A is the quantum yield of acetone disappearance. Φ_A cannot be measured directly, and it can be calculated only when $\Phi_{CH_4}=0$, i.e., when the intensity is high and preferably when the pressure is low. Under such conditions

$$\Phi_A = 2 \Phi_{C_2H_6} - \Phi_{CO.} \tag{40}$$

Taking the data preceding Eq. (38) and making the proper substitutions in Eq. (39), one finds either

$$\pm 1.377(\phi_{3130} - 0.27) = \phi_{2537} - 0.44.$$
 (41)

If the minus sign is chosen, $\phi_{2537} = 0.13$ if $\phi_{3130} = 0.5$. Since the quantum yields of acetone disappearance are sometimes greater than 0.5 at both 3130 and 2537A,⁸ the values of ϕ_{3130} and ϕ_{2537} must both be greater than 0.5. The positive sign is the only one which leads to a physically acceptable result. Hence,

$$\phi_{2537} = 1.377 \phi_{3130} + 0.068. \tag{42}$$

If $\phi_{2537}=1$, $\phi_{3130}=0.68$. The accuracy of this figure is difficult to estimate, but it should be within ± 0.15 and indicates that the primary quantum yield at 3130A is significantly less than 1. This is in general agreement with the existence of fluorescence. However, ϕ_{3130} must be temperature dependent, as indicated by the fluorescence and photo-chemical data,¹⁰ and reach a value close to unity at 100°C.

Another approximation may be made to arrive at a value of ϕ . In earlier work⁸ it was assumed that at relatively low pressures reactions (12) and (13) occurred mainly on the walls, a conclusion supported by the work of Anderson and Rollefson,^{21,22} whereas the reformation of acetone was a rapid reaction which occurred mainly in the gas phase. The following data are taken from previous work⁸ at 25°C and a

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²¹ H. W. Anderson and G. K. Rollefson, J. Am. Chem. Soc. 63, 816 (1941). ²² E. W. R. Steacie and B. de B. Darwent, J. Chem.

²² E. W. R. Steacie and B. de B. Darwent, J. Chem. Phys. 16, 230 (1948) have shown that the character of the wall surface does not affect the C_2H_6/CO ratio. This would not have been expected if wall recombinations of free radicals occur. On the other hand, for rapid reactions, such as CH_4CO+CH_3CO with a very low activation energy the character of the walls may not be too important. The data in the region where wall reactions may be important do not lead to very definite conclusions. On the other hand, it is impossible to explain the increase in C_2H_6/CO ratio at low pressures without heterogeneous formation of biacetyl.

TABLE III. Summary of various constants.*

Constant	$T = 0^{\circ}C$	$T = 25^{\circ}C$	<i>T</i> =120°C
\$ 3130	0.5	0.7 (100 mm) 0.8 (25 mm)	1.0
Φ2537 <i>a</i> 3130	1.0	1.0 0.07 0.22	1.0
$\frac{k_{2}}{k_{3}}/k_{5}^{2}$ $k_{3}k_{6}/k_{4}^{2}$		1.37×10 ²⁷	9.8×10 ²⁴ 2.0
${k_1/k_2^{1\over 2}} {k_4^2/k_2k_3}$		4.8 ×10 ⁻⁸ 1.1	

* The energy of activation for reaction (5) is 6500 cal. (see reference 12).

pressure of 25 mm:

$$\frac{\Phi_{C_2H_6}}{M_2} \frac{\Phi_{Co}}{M_2} \frac{I_a}{10} \frac{I_a}{10} \frac{1}{10} \frac{1}{10}$$

where k_{2}' and k_{3}' are the constants for wall combination to form $(COCH_{3})_{2}$ and $(CH_{3})_{2}$, respectively. Placing $\phi_{2537}=1$, ϕ_{3130} is found to be 0.78, a reasonably good check with the value found from Eq. (42). Perhaps ϕ should increase with decrease in pressure (see below).

Returning to Eq. (39) and assuming $\phi_{2537} = 1$ (which is a very reasonable assumption from all standpoints), it is seen that

$$k_4^2/k_2k_3 = 1.1. \tag{44}$$

The constants in Eq. (44) are all constants for association reactions of radicals and would be expected to have small temperature coefficients. If it is assumed tentatively that $k_4^2/k_2k_3 = 1.1$ at 0°C, one can make use of data from earlier work⁸ at a pressure of 110 mm to calculate ϕ_{3130} at that temperature. The following quantum yields were used: $\Phi_{C_2H_6} = 0.19$, $\Phi_{CO} = 0.045$. From Eq. (39) one finds $\phi_{3130} = 0.51$ at 0°C. This is a further indication that ϕ is temperature dependent.

A possible explanation of the temperature dependence of ϕ may be offered. At 2537, where $\phi = 1$, direct dissociation of the acetone molecule may be assumed to occur upon absorption of radiation. At 3130 the following steps may be visualized:

 $\mathbf{A} + h\mathbf{v} = \mathbf{A}' \qquad ; \text{ rate} = I_a, \qquad (45)$

 $A' = CH_3 + COCH_3; \text{ rate} = k_9(A'), \quad (46)$

$$A' + A = 2A$$
; rate = $k_{10}(A')(A')$. (47)

A' might undergo other processes, such as fluorescence, but these need not be considered here. This leads to the definition of ϕ as follows:

$$\phi = 1/(1+k_{10}(A)/k_9). \tag{48}$$

 ϕ would thus be pressure dependent. Since fluorescence would be a competing process for (46), it cannot be stated that ϕ should become unity at zero pressure, but the trend toward increased values at lower pressures seems to be definite. Data on this point are inadequate. If k_{10} is assumed to have zero activation energy, an activation energy for k_9 is estimated to be about 5000 cal. Thus ϕ would be very close to unity at temperatures above 100°C, as required by the data.

Little can be said about a. From Eq. (36) and the data preceding Eq. (38) one can show that

$$a_{3130} = (a_{2537} - 0.17)/0.68. \tag{49}$$

Thus if a_{2537} is given the value previously calculated⁸ of 0.22, $a_{3130} = 0.073$ at 25°C. The dependence of *a* on temperature cannot be estimated from present data.

As pointed out recently by Steacie and Darwent,²² the C₂H₆/CO ratio at 25°C obtained by various authors increased with increase in I_a . This is in accord with the mechanism proposed in the present article. If the values of ϕ and a at 3130A are accepted as 0.70 and 0.073, respectively, the maximum value of C_2H_6/CO at infinite intensity would be 5.2. At 2537 with $\phi = 1.0$ and a = 0.22, C₂H₆/CO would have a maximum value of 2.8. To account for the ratio of 3.6 observed by Anderson and Rollefson,²¹ a would have to be 0.18 if $\phi_{2537} = 1$. If the mercury sensitized reaction follows the same pattern, a_{2537} would have to be 0.14 to account for the results of Steacie and Darwent. However, there is sound reason to believe that a for the sensitized reaction should be somewhat lower than for the unsensitized reaction. In view of the type of arc used, Anderson and Rollefson²¹ probably were also dealing at least partially with a mercury sensitized reaction. When an excited mercury atom collides with a CH₃COCH₃ molecule to form CH₃+CH₃CO, the laws of conservation of energy and conservation of momentum must be obeyed. Thus part of the energy will be imparted

to the mercury atom as kinetic energy, and the kinetic energy of the CH₃CO radical, as well as possibly its vibrational energy, may be appreciably lower than that of a radical produced by absorption of 2537A radiation directly by an acetone molecule. In the absence of further information we may accept $\phi_{2537} = 1$, $a_{2537} = 0.22 \pm 0.05$ at 25°C.

In conclusion, it is well to give a summary of the various constants concerning the mechanism which have been evaluated.

The mechanism proposed in this article accounts for the following points:

(a) The variation of the C_2H_6/CO ratio with pressure, with intensity, with temperature, and with wave-length;

(b) the increase in the CH_4/C_2H_6 ratio with decreasing intensity and increasing pressure;

(c) variation of quantum yields of C_2H_6 , CO, and CH₄ with temperature and pressure;

(d) the effect of wave-length on the CO yield;

(e) the formation of all known products;

(f) qualitatively for fluorescence and its variation with temperature. This point and its relationship to primary quantum yield merit further study.

It is believed that the mechanism does not disagree with any experimental facts so far available. In particular it agrees qualitatively with Fig. 2 of the second article by Spence and Wild,⁵ who were the first to point out that the C_2H_6/CO ratio really falls on a family of curves, one for each pressure as a function of intensity.

The mechanism makes no pretense of describing acetone decomposition except in the early stages before products have been allowed to accumulate. With large percentage decomposition there must be secondary reactions which would change the composition of the gaseous products. Also the effect of the walls has not been included in detail. Such effects are almost certainly not of importance except at pressures below 50 mm and in any case could not be included easily in any quantitative theory. Many of the effects previously ascribed to the walls are undoubtedly due to variations in intensity and in pressure. The importance of obtaining data in such a fashion that the number of quanta absorbed per unit volume per second is as constant as possible is obvious from the nature of the mechanism.

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The Vapor Pressure and Heat of Sublimation of Graphite*

LEO BREWER, PAUL W. GILLES,** AND FRANCIS A. JENKINS

Department of Chemistry, Radiation Laboratory,*** and Department of Physics, University of California, Berkeley (Received April 19, 1948)

The heat of sublimation of graphite and the heats of dissociation of CO and C_2 , which have been the subject of much controversy in recent years, have been unambiguously established by the direct determination of the total vapor pressure of graphite by an equilibrium effusion method and by the determination of the partial pressure of $C_2(gas)$ in equilibrium with graphite.

The heat of sublimation of graphite to C(g) is found to be $\Delta H_0 = 170.39 \pm 0.20$ kilocalories per mole at 0°K. The heat of sublimation of graphite to $C_2(g)$ is found to be $\Delta H_0 = 233.1 \pm 7$ kilocalories per mole. The heats of dissociation of C_2 and CO have been shown to be 4.7 ± 0.3 and 11.109 ± 0.01 electron volts, respectively. The accommodation coefficient of carbon gas on graphite at high temperatures is found to be about 0.3 and vaporized carbon gas is shown to be in the ³P ground electronic state.

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^{**} du Pont Fellow in Chemistry, 1946-1947; present address: Chemistry Department, The University of Kansas, Lawrence, Kansas.

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