close to the corresponding values recorded for CCl_2FCClF_2 (extrapolated from 25 to 20°) of MR 26.12 and AR_F 1.13. The most important difference is, as expected, between the freezing points, *i. e.*, +14.2° for the asymmetrical CCl_3CF_3 and −36.4° for the symmetrical CCl_2FCClF_2.

Conclusion.—The experimental data confirm the contention that fully halogenated fluorides differ little in most of their physical properties, but markedly in their freezing points. The boiling point of an asymmetrical compound is very slightly lower, and its freezing point is markedly higher, than those of its symmetrical isomer.

Acknowledgment.—We wish to thank Dr. L. A. Bigelow for his very helpful spirit of collaboration in trying to clear the discrepancy between his data and ours.

Summary

Improved physical data are listed for $CCl_2{=}CF_2$, CCl_3CClF_2, CCl_2BrCF_2Br, $CClFBrCClFBr$ and CCl_3CF_3. The boiling point presented by Bigelow[2] for $CCl_2{=}CF_2$ was not duplicated. The method of predicting physical properties of fully halogenated fluorides by general analogy is sustained.

COLUMBUS, OHIO RECEIVED MAY 22, 1940

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF ROCHESTER]

Photochemical Studies. XXXI. A Systematic Study of the Near Ultraviolet Photochemical Decomposition of Acetone

BY DONALD S. HERR AND W. ALBERT NOYES, JR.

The photochemical decomposition of acetone vapor has been the subject of numerous investigations.[1] Much speculation concerning both primary and secondary processes has appeared in the chemical literature. It is quite evident, however, that a systematic study covering several variables, particularly intensity, pressure and temperature should be made as a prerequisite to further discussion concerning the mechanism of this reaction. This work has been performed with the hope of supplying some of the essential data.

An appreciable fraction of the photochemical decomposition of acetone proceeds by the over-all equation[2,3,4,5]

$$CH_3COCH_3 = C_2H_6 + CO \qquad (1)$$

Indeed, many quantum yields for this reaction have been based on analyses for carbon monoxide, the assumption being made that one molecule of acetone disappears for each molecule of carbon monoxide formed. However a second reaction takes place to a considerable extent at temperatures up to 60°.[6]

$$2CH_3COCH_3 = C_2H_6 + (CH_3CO)_2 \qquad (2)$$

Additional products not indicated by reactions (1) and (2) may be found at elevated temperatures, but these are to be ascribed to secondary reactions involving methyl radicals. Thus methane is found under such conditions,[7,8] but practically none is formed under conditions used in the present experiments.

A polymerization, supposedly aided by the presence of water, has been reported.[5] Evidence for this reaction is not satisfactory. Biacetyl, one of the products of reaction (2), is known to polymerize under some conditions.

The general conclusion may be drawn both from previous work and from the data herein presented that reactions (1) and (2) account within experimental error for all of the photochemical acetone decomposition at temperatures below 150° and in wave length regions which have hitherto been explored. In what follows this conclusion is accepted as a basis for discussion.

I. Experimental

The source of radiation was a high pressure mercury arc lamp. In order to obtain monochromatic 3130 Å. radiation, a thin silver film and a cobalt–nickel sulfate solution[9] 5 cm. in thickness were used. The spectrum transmitted by this combination was photographed and over 95%

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[1] For a recent summary see P. A. Leighton, *J. Phys. Chem.*, **42**, 749 (1938). The literature will not be cited in detail at this time, although reference to much of it will appear during the discussion.

[2] Berthelot and Gaudechon, *Compt. rend.*, **155**, 207 (1912).

[3] Bowen and Watts, *J. Chem. Soc.*, 1607 (1926).

[4] Kirkbride and Norrish, *Trans. Faraday Soc.*, **123**, 407 (1931).

[5] Damon and Daniels, THIS JOURNAL, **55**, 2363 (1933).

[6] Barak and Style, *Nature*, **135**, 307 (1935); Spence and Wild, *ibid.*, **138**, 206 (1936).

[7] Leermakers, THIS JOURNAL, **56**, 1897 (1934).

[8] Taylor and Rosenblum, *J. Chem. Phys.*, **6**, 119 (1938).

[9] Bäckström, *Naturwiss.*, **21**, 251 (1933).

of the radiation was found to lie in the group of lines near 3130 Å.

To obtain 2537 Å., the silver film was removed, and a chlorine gas filter at a pressure of 1 atmosphere and 5 cm. in length was inserted.

The method of gas analysis has been described by Manning.[10] Since the sole gaseous products were ethane and carbon monoxide together with small amounts of methane, removal of gases uncondensed by liquid nitrogen provided a means of separating the carbon monoxide and methane almost, but not quite, completely from the ethane. The acetone was vaporized and recondensed at least twice in order to ensure that the carbon monoxide was completely removed by the Toepler pump.

The ethane was next removed by the Toepler pump while the acetone was condensed by a pentane mush at a temperature of about −132°.

The amounts of carbon monoxide and of ethane could be used to calculate the amount of biacetyl, if it is assumed that reactions (1) and (2) are the sole modes of decomposition. Thus if N_{CO} and $N_{C_2H_6}$ are the numbers of molecules of carbon monoxide and of ethane, respectively, the number of molecules of biacetyl is

$$N_{(CH_3CO)_2} = N_{C_2H_6} - N_{CO} \qquad (3)$$

and the total number of molecules of acetone disappearing is

$$\begin{aligned} N_{CH_3COCH_3} &= N_{CO} + 2(N_{C_2H_6} - N_{CO}) \qquad (4) \\ &= 2N_{C_2H_6} - N_{CO} \qquad (5) \end{aligned}$$

Numbers of quanta absorbed were determined by reference to the uranyl oxalate actinometer.[11] A photoelectric cell with quartz window was calibrated with this actinometer for each wave length. The actual measurements were made by the photoelectric cell. It should be pointed out that the quantum yield of carbon monoxide formation at 25° and a pressure of about 100 mm. given in this article agrees well within experimental error with measurements made using a thermopile calibrated with a standard source of radiation.[12]

The quantum yields should have absolute accuracies of better than 10% and relative values should be valid within better than 5%. With low light absorption the chief error is probably in measurements of ethane and of carbon monoxide. With larger amounts of decomposition the chief error probably resides in measurements of light intensity. Calculations of the numbers of molecules of acetone disappearing by equation (5) are subject to greater uncertainties than the individual values for ethane and for carbon monoxide.

Some question may be raised as to the validity of the gas analysis due to the solubilities of the product gases (particularly ethane) in the solidified acetone. A 400-cc. bulb was sealed to the line, thus increasing the amount of acetone to be condensed to approximately twice its former value. The quantum yields, as well as the ratio of ethane to carbon monoxide, were unaffected by this procedure.

The temperature of the reaction vessel was varied by surrounding it with a bath which was jacketed and hand regulated. Temperature control was better than one degree.

In determining the effect of pressure on the quantum yields it must be kept in mind that, in order to avoid simultaneous change in two variables, it is necessary to increase the incident intensity as the pressure is lowered so that the number of quanta absorbed per cubic centimeter per second remains constant. In the data on the effect of pressure the intensity absorbed per unit volume was kept constant.

II. Results

It does not seem desirable to present all of the data in detail. Table I shows runs made near room temperature in which the pressure and the incident intensity were both varied. These data and all of the remaining data are shown in graphs.

TABLE I

EFFECT OF PRESSURE ON QUANTUM YIELD OF ACETONE DECOMPOSITION

$T = 25 \pm 1°$; wave length, 3130 Å.; quanta absorbed per second, 5×10^{13}; volume of line, 352.5 cc.; volume of vessel, 50 cc.

Acetone press., cm.	Time of irradiation, min.	Quantum yield of CO formation	$\frac{N_{C_2H_6}}{N_{CO}}$	Quantum yield of	
				C_2H_6 formation	Acetone decompn. (eq. (5))
16.2	180	0.115	1.45	0.167	0.22
10.7	272	.109	1.67	.182	.26
5.0	240	.108	2.03	.219	.33
2.55	291	.090	2.63	.236	.38
2.3	240	.089	2.71	.241	.39
1.23	240	.082	3.49	.286	.49

Data at still lower pressures could not be obtained without reducing the number of quanta absorbed per second.

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[10] Manning, THIS JOURNAL, **56**, 2589 (1934).

[11] Leighton and Forbes, *ibid.*, **52**, 3139 (1930).

[12] These determinations were made by one of us (W. A. N., Jr.) at Brown University in 1931. They have been referred to (Ells and Noyes, THIS JOURNAL, **61**, 2493 (1939)).

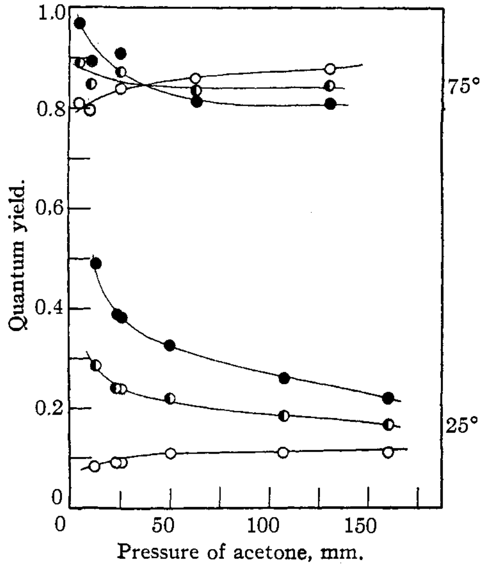

Fig. 1.—Quantum yields at 3130 Å. and I_a = 10: O, Φ for CO formation; ◑, Φ for ethane formation; ●, Φ for acetone decomposition; ⊕, Φ for CO = Φ for ethane = Φ for acetone.

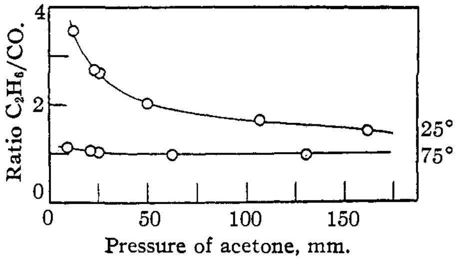

Fig. 1a.—Ratios at 3130 Å. and I_a = 10.

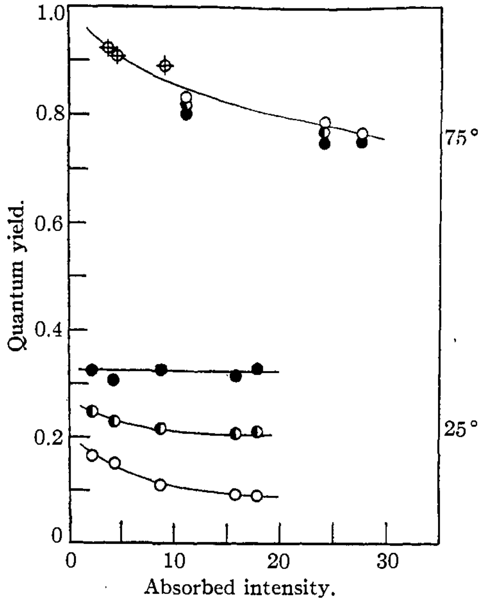

Fig. 2.—Quantum yields at 3130 Å. and 50 mm.

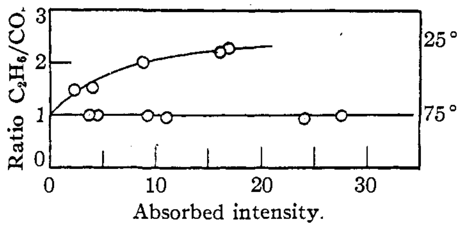

Fig. 2a.—Ratios at 3130 Å. and 50 mm.

The figures show the data graphically. Quantum yields of carbon monoxide formation, of ethane formation, and of acetone disappearance, as well as the ratios of ethane to carbon monoxide, are shown as functions of pressure, intensity, and temperature. These graphs are largely self-explanatory, and reference to them will be made only in the discussion of results.

III. Discussion of Results and Conclusions

The primary process in acetone both at wave lengths 3130 and 2537 Å. seems to be a dissociation into free radicals according to the equation

$$CH_3COCH_3 + h\nu = CH_3CO + CH_3 \qquad (6)$$

This primary process is strongly indicated by the work of Gorin,[13] who has shown that acetone in the presence of iodine yields methyl iodide and acetyl iodide and that nearly one molecule of acetone disappears per quantum absorbed. Some uncertainty may exist in the interpretation of Gorin's experiments since no information exists concerning the possible reaction of excited acetone molecules with molecular iodine. Some evidence (to be published later) from a study of fluorescence leaves some doubt as to whether the quantum yield of the primary process is really unity. The primary quantum yield must, however, be very high, and we feel safe in basing our interpretation on such an assumption.

In discussing the data it seems best, for the sake of clarity, to adopt the doubtful procedure of postulating a mechanism which seems adequate to explain most of the facts and then relate the facts to the mechanism.

In addition to primary process (6) whose rate will be proportional to the absorbed intensity, I_a, and the quantum yield of the primary process, ϕ, the following secondary processes seem necessary:

(1) A spontaneous dissociation of a certain fraction a of the acetyl radicals due to energy of excitation retained after the primary process.

$$COCH_3 = CH_3 + CO; \; a\phi I_a \qquad (7)$$

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[13] Gorin, *J. Chem. Phys.*, **7**, 256 (1939).

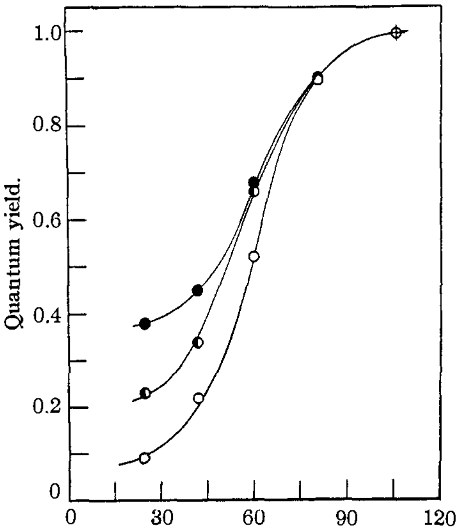

Fig. 3.—Quantum yields at 3130 Å., 25 mm. and I_a = 10.

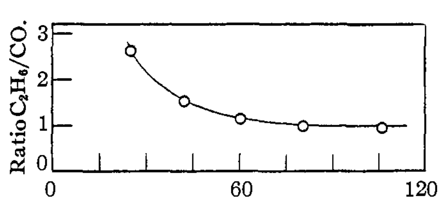

Fig. 3a.—Ratios at 3130 Å., 25 mm. and I_a = 10.

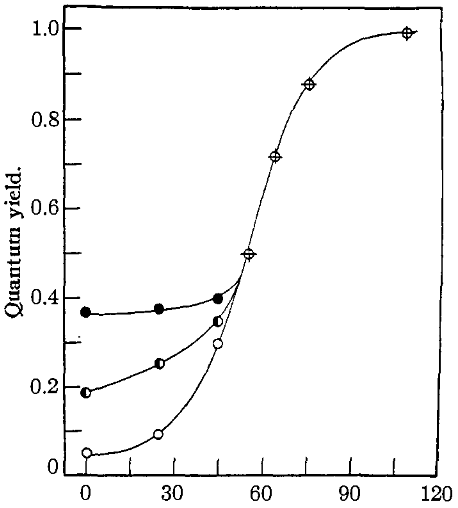

Fig. 4.—Quantum yields at 3130 Å., 110 mm. and I_a = 10

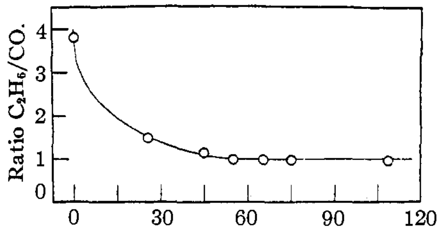

Fig. 4a.—Ratios at 3130 Å., 110 mm. and I_a = 10.

This step is necessitated by the fact that the quantum yield of carbon monoxide formation varies with the wave length (about 0.1 at 3130 Å., about 0.25 at 2537 Å., and about 0.50 at 1850–2000 Å.) (see Figs. 1 and 5). Thus *a* will be expected to increase at decreasing wave length and should be independent of temperature.

Equation (7) is doubtless a crude method of expressing a complex situation in which collisions may play some part. If all of those acetyl radicals which do not decompose at once according to (7) undergo other secondary reactions and in particular if the activation energy for

$$\mathrm{CH_3CO + I_2 = CH_3COI + I} \qquad (8)$$

is low, the assumption of (7) is compatible with the results of Gorin,[13] who found some carbon monoxide to be formed even in the presence of iodine.

(2) A first order decomposition of acetyl radicals.

$$\mathrm{CH_3CO = CH_3 + CO};\ k_2(\mathrm{Ac}) \qquad (9)$$

(Ac) represents the concentration of acetyl radicals.

Since the quantum yields of carbon monoxide formation and of acetone disappearance increase rapidly with temperature (Figs. 3 and 4) and since little biacetyl is formed at temperatures over 60°,[14] it is necessary to conclude that (9) has a rather high activation energy. Gorin[13] estimates 17 kcal. as the activation energy of this step and 18 kcal. is compatible with the data in this article, although it is impossible to calculate a very accurate value of this quantity, and the uncertainty is probably as much as 5 kcal.

As the temperature increases, (9) becomes more important than (7) as a source of carbon monoxide so that the variation of yield with wave length should become less pronounced. This again agrees reasonably well with earlier data,[5,15,16] although some discrepancies exist in the literature.

(3) A diffusion of acetyl radicals to the walls with resultant production of biacetyl

$$\mathrm{COCH_3} \overset{\text{walls}}{=} {}^1/_2(\mathrm{CH_3CO})_2;\ k_3(\mathrm{Ac})/p \qquad (10)$$

p is the total pressure (*i. e.*, the pressure of the acetone). k_3 will be proportional to the square

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[14] Spence and Wild, *J. Chem. Soc.*, 352 (1937).

[15] Norrish, Crone and Saltmarsh, *J. Chem. Soc.*, 1456 (1934).

[16] Howe and Noyes, THIS JOURNAL, **58**, 1404 (1936).

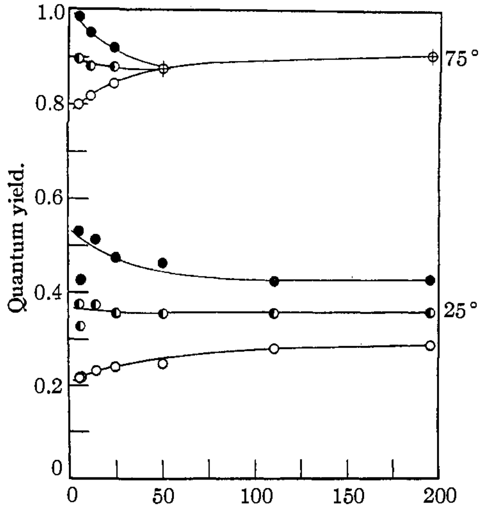

Fig. 5.—Quantum yields at 2537 Å. and I_a = 10.

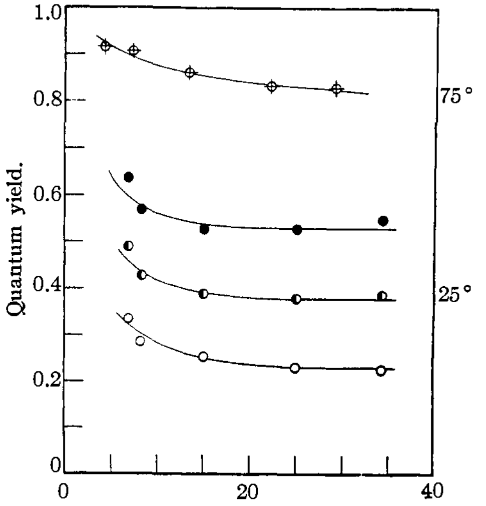

Fig. 6.—Quantum yields at 2537 Å. and 50 mm.

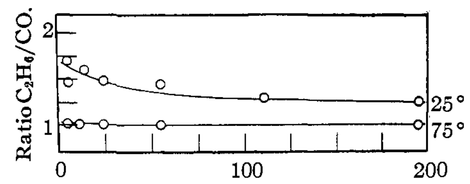

Fig. 5a.—Ratios at 2537 Å. and I_a = 10.

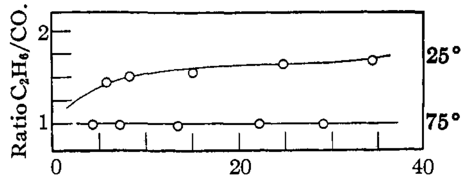

Fig. 6a.—Ratios at 2537 Å. and 50 mm.

root of the absolute temperature. Its magnitude may be estimated from the mean distance of diffusion to the walls (about 1 cm.) to be between $0.05 \times 10^2\ T^{1/2}$ and $0.1 \times 10^2\ T^{1/2}$ if the pressure, p, is expressed in millimeters and the unit of time is the second.[17]

Biacetyl is known to be formed[6,18,19] both from chemical analysis and from the spectrum of the fluorescence. Since the yield of ethane increases relative to the yield of carbon monoxide as the pressure is lowered when the absorbed intensity is kept constant, the yield of biacetyl calculated from equation (3) must increase also. This seems to be fairly conclusive evidence that a large fraction of biacetyl is formed on the walls. It is significant that the ratio of ethane to carbon monoxide reaches unity at higher temperature when the pressure is low than when it is high (Figs. 3 and 3(a)).

However, since the ratio of ethane to carbon monoxide increases slightly with the intensity at constant pressure (Figs. 2(a) and 6(a)), it is necessary to conclude that there is some homogeneous gas phase combination of acetyl radicals to give biacetyl. This reaction is probably relatively unimportant, and its introduction would complicate the expressions to be derived later to the point where little meaning could be attached to the constants. Therefore this homogeneous step is omitted to a first approximation.

(4) A homogeneous gas phase reaction between methyl and acetyl radicals to form acetone

$$CH_3 + COCH_3 = CH_3COCH_3;\ k_4(Ac)(Me) \quad (11)$$

where (Me) represents concentration of methyl radicals. The rate of (11) must be rapid and the activation energy must be low as this reaction is assumed to be responsible for the low quantum yield of acetone disappearance (see Figs. 1–7). While third bodies may be necessary for its completion, their concentration does not seem to be decisive in determining the rate.

One other suggestion has been made to explain the low quantum yield of acetone disappearance.[20]

$$CH_3 + (CH_3CO)_2 = CH_3COCH_3 + COCH_3 \quad (12)$$

Reaction (12) may occur, but evidence to be presented later will indicate that it is too slow to be

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[17] See, for example, P. A. Leighton, "The Determination of the Mechanism of Photochemical Reactions," Hermann et Cie., Paris, 1938, p. 13.

[18] Matheson and Noyes, THIS JOURNAL, **60**, 1857 (1938).

[19] Matheson and Zabor, *J. Chem. Phys.*, **7**, 536 (1939).

[20] Taylor and Jungers, *Trans. Faraday Soc.*, **33**, 1353 (1937).

of importance in the present connection. Also the yield should depend on time of exposure if (12) is important. An experiment was tried in which the yield after twenty minutes was compared with that after three hours. No difference was noted. The rate of (12) would have to be exceedingly rapid to prevent such a variation from being detected. It is possible, however, that part of the rather rapid increase of yield with temperature may be due to the fact that biacetyl is formed to a smaller extent at higher temperatures.

(5) A diffusion of methyl radicals to the walls with the resultant production of ethane.

$$CH_3 \overset{\text{walls}}{=} {}^1/_2C_2H_6;\ k_5(\text{Me})/p \qquad (13)$$

The constant k_5 will be larger than k_3 due to the lower mass of the methyl radical. The magnitude of k_5 will probably be between 0.1×10^2 $T^{1/2}$ and 0.15×10^2 $T^{1/2}$.[17] Once more the possibility of a homogeneous reaction leading to ethane cannot be ignored, but it need not be considered at the present time.

Equations for the steady states of acetyl and of methyl radicals may be written, respectively,

$$(1 - a)\phi I_a = k_2(\text{Ac}) + k_3(\text{Ac})/p + k_4(\text{Ac})(\text{Me}) \qquad (14)$$

$$(1 + a)\phi I_a + k_2(\text{Ac}) = k_4(\text{Ac})(\text{Me}) + k_5(\text{Me})/p \qquad (15)$$

and hence

$$2a\phi I_a + 2k_2(\text{Ac}) + k_3(\text{Ac})/p = k_5(\text{Me})/p \qquad (16)$$

The quantum yield of carbon monoxide formation is

$$\Phi_{CO} = a\phi + k_2(\text{Ac})/I_a \qquad (17)$$

and that of ethane formation is

$$\Phi_{C_2H_6} = {}^1/_2k_5(\text{Me})/pI_a \qquad (18)$$

The number of molecules of acetone disappearing per quantum absorbed is

$$\Phi_A = 1 - k_4(\text{Ac})(\text{Me})/I_a \qquad (19)$$

From these relationships it is possible to show that

$$\frac{\Phi_{CO} - a\phi}{2(\Phi_{C_2H_6} - \Phi_{CO})p} = k_2/k_3 \qquad (20)$$

Equation (20) must be used with the knowledge that it ignores possible homogeneous reactions leading to biacetyl and to ethane. It may be used to evaluate a by equating left-hand members for two pressures. The difference in the denominator renders the accuracy small, although the results are quite consistent. ϕ is assumed to be one.

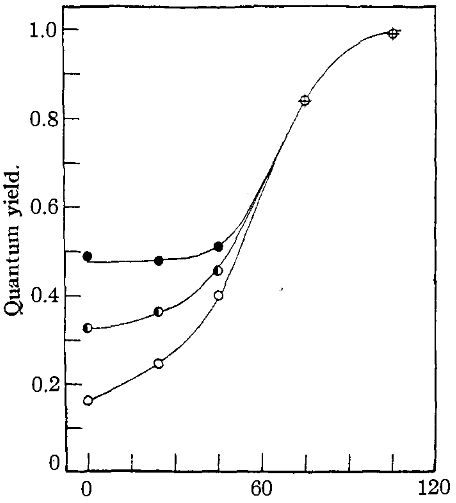

Fig. 7.—Quantum yields at 2537 Å., 25 mm. and I_a = 10.

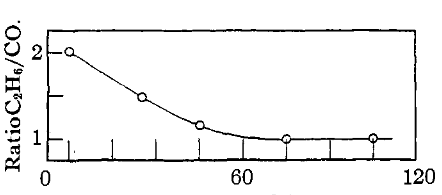

Fig. 7a.—Ratios at 2537 Å., 25 mm. and I_a = 10.

As pointed out above a must increase with decrease in wave length in order to explain the quantum yield of carbon monoxide formation. The average value found by using successive pressure intervals at 3130 Å. is 0.067 while at 2537 Å. it has become 0.222. Accurate analyses for ethane are not available for the wave length region 1850–2000 Å.,[16] but the value of a must be about 0.5.

On the other hand, the ratio k_2/k_3 should be independent of wave length, and this is found to be true within the errors of the determination of this ratio. The average of k_2/k_3 at 25° using data at both 3130 and 2537 Å. is 2.95×10^{-3}.

To illustrate that equation (20) fits the data with considerable fidelity, ratios of ethane to carbon monoxide have been calculated using the above average constants, with results shown in Table II.

TABLE II

COMPARISON OF FOUND AND CALCULATED RATIOS OF ETHANE TO CARBON MONOXIDE AT 25°

3130 Å.			2537 Å.		
Pressure, mm.	Calcd.	Found	Pressure, mm.	Calcd.	Found
162	1.44	1.45	195	1.21	1.24
107	1.61	1.67	110	1.32	1.29
50	2.28	2.03	50	1.38	1.44
25.5	2.69	2.63	25	1.51	1.50
23	2.82	2.71			
12.3	3.50	3.49			

If it is assumed that k_3 is proportional to the square root of the absolute temperature, it is possible to calculate an activation energy for k_2 from determinations of the ratio k_2/k_3 at several temperatures. Unfortunately, equation (20) breaks down when the quantum yields of ethane and of carbon monoxide are equal, so that it is possible to calculate the activation energy for k_2 over a small temperature interval only. As pointed out above a value of $E_2 = 18$ kcal. is consistent with the data. The steric factor for k_2 can be calculated from the absolute value of k_3, the constant for diffusion of acetyl radicals to the walls. The magnitude of the latter is not known with high precision, but the steric factor for k_2 is found to lie between 10^{13} and 10^{14}.

Since k_2, k_3, a, and I_a are either known or can be estimated, it is possible from equation (17) to obtain the steady-state concentration of acetyl radicals. The steady-state concentration of methyl radicals may now be obtained from equation (16). Since values of Φ_A are known, it is possible now to obtain k_4 from equation (19). The actual values of k_4 depend on both k_3 and k_5, but if the figures cited above are used, it is found that k_4 lies near the upper limit of reasonable values for bimolecular rate constants and that the heat of activation for the reaction between methyl and acetyl radicals to form acetone must be very small indeed.

Some additional consideration should be given to the variation of the ratio of ethane to carbon monoxide with absorbed intensity (see Figs. 2(a) and 6(a)). As might be expected, more variation is found at 3130 than at 2537 Å., since a larger fraction of the carbon monoxide is formed during the primary act at the latter wave length. As the temperature is raised the variation is also less since the amount of biacetyl formed is lower (Figs. 3(a) and 4(a)).

These facts necessitate the introduction of homogeneous reactions between acetyl radicals and also between methyl radicals, but little more need be said concerning this matter since the introduction of these steps will obviously provide a qualitative explanation of the facts even though quantitative calculations cannot be made.

One further step, suggested by Gorin,[13] needs to be considered

$$CH_3 + CH_3CO = C_2H_6 + CO \qquad (21)$$

If (21), (22), and (23) are used in place of (9), (10), and (13), the yields and the ratio of ethane to carbon monoxide all become independent of intensity as well as of pressure.

$$2CH_3CO = (CH_3CO)_2 \qquad (22)$$

$$2CH_3 = C_2H_6 \qquad (23)$$

Indeed, if third bodies are necessary for the association reactions the effect of pressure would be the opposite of that found experimentally (see Figs. 2, 2(a), 6, and 6(a)).

However, the small variation of the ratio of ethane to carbon monoxide with intensity when the pressure is over 100 mm. may mean that reaction (21) takes place to some extent when wall reactions are unimportant.

A few remarks concerning the significance of the a term are pertinent. If the energy required to split an acetone molecule into a methyl radical and an acetyl radical is 70 kcal. per mole, at 3130 Å. some 21 kcal. per *einstein* are absorbed in excess of this amount. At 2537 Å. the excess is about 43 kcal., and at 1900 Å. the excess is about 80 kcal. The distribution of the excess energy between the two free radicals cannot be estimated since nothing is known concerning either vibration frequencies or electronic states of these radicals. It is evident that a simple picture is not adequate. The amount of energy in the acetyl radical may be decisive in determining a, but it seems more probable that a certain fraction of the acetone molecules will dissociate directly into methyl radicals and carbon monoxide molecules following suggestions previously made.[15,16] If this is true, the nature of the hyper-surface representing the excited state and of its interaction with the two repulsive surfaces leading to dissociation by (6) and into two methyl radicals will be decisive in determining a. There is nothing inherently absurd in the mechanism as outlined, but further speculation concerning a in the present state of our knowledge would be unwarranted.

Summary

1. The quantum yields of carbon monoxide formation, of ethane formation, and (indirectly) of acetone disappearance have been determined for the photochemical decomposition of acetone at wave lengths 3130 and 2537 Å. as functions of pressure, temperature, and absorbed intensity.

2. The variation of quantum yield with wave length necessitates either the assumption that a certain fraction of the acetyl radicals decompose spontaneously as the result of energy retained at the moment of dissociation of the acetone

molecule or the assumption that a certain fraction of the acetone molecules dissociate directly into two methyl radicals and carbon monoxide. The fraction is a function of the absorbed wave length.

3. A mechanism is advanced to account for the facts.

4. Biacetyl is formed largely as a result of a wall reaction, although some homogeneous reaction between acetyl radicals must occur.

5. The best value for the energy of activation for dissociation of the acetyl radical into carbon monoxide and a methyl radical is about 18 kcal.

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[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY AND PHYSICS OF THE PENNSYLVANIA STATE COLLEGE]

The Heat Capacity and Entropy, Heats of Fusion and Vaporization and the Vapor Pressure of Isobutane

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The comparison of the entropy values for gaseous ethane obtained by use of the third law with those calculated from the spectroscopic data has indicated that the potential hindering the internal rotation of the methyl group is 3150 cal.[1] Similarly a potential of 4200 cal. hindering the internal rotation of the methyl groups in tetramethylmethane (neopentane) has been inferred.[2,3,4] From these results Pitzer has interpolated the potential hindering the internal rotation of the three methyl groups in isobutane to be 3800 cal.[5] The following paragraphs describe an investigation of the thermal properties of isobutane extending down to 11.9°K. which shows the hindering potential to be 3870 cal. if certain assumptions about the vibration spectrum are valid.

Preparation and Purification of Isobutane.—Tertiary butyl alcohol, purified by distillation followed by several recrystallizations to constant melting point (m. p. 23.83–23.91°), was dehydrated at 300 to 310° by passing it through a horizontal tube 80 cm. long, 2.1 cm. in diameter, packed for 76 cm. with a mixture of 90% alumina (80 mesh) and 10% Pyrex glass wool. The effluent vapor was passed first through a condenser to remove as much water as possible, next through three scrubbers filled with 25% sodium hydroxide and lastly through a tube 40 cm. long, 1.8 cm. in diameter and packed with dry alumina. The vapor was collected in a series of solid carbon dioxide–acetone traps. The alcohol was added at a rate of 100 cc. per hour. A total of 650 cc. of crude liquid isobutylene was obtained—a yield of 85%.

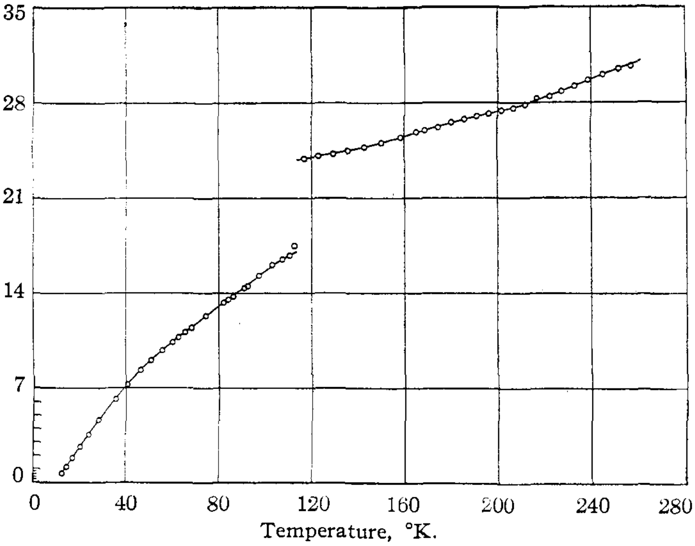

Fig. 1.—Molal heat capacity of isobutane.

Two hundred cc. of the isobutylene thus prepared was hydrogenated over 12 cc. (36 g.) of Raney nickel previously washed five times with *t*-butyl alcohol. The hydrogen pressure was kept constant at 1000 lb./sq. in. (67 atm.). At 16° the hydrogenation went to completion in two and one-half hours. After the reaction was completed, the material was condensed into a high pressure cylinder. The yield was 84.7% of isobutane.

The crude isobutane was first purified by passing it through three wash bottles of concentrated sulfuric acid, then through three sulfuric acid scrubbing towers, a potassium hydroxide tube and a phosphorus pentoxide tube. The condensed gas was then fractionated through the laboratory low temperature column. The sample was dried over phosphorus pentoxide before being condensed in the sample bulb. Alternate cooling to liquid air temperature, with evacuation to 10^{-6} mm. of mercury, and thawing removed the last traces of air before the bulb was sealed off and weighed ready for introduction of the sample into the apparatus in the customary manner.[2]

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[1] Kemp and Pitzer, THIS JOURNAL, **59**, 276 (1937).

[2] Aston and Messerly, *ibid.*, **58**, 2354 (1936).

[3] Aston, Siller and Messerly, *ibid.*, **59**, 1743 (1937).

[4] Pitzer, *J. Chem. Phys.*, **5**, 469 (1937).

[5] Pitzer, *ibid.*, **5**, 473 (1937).