pendent equations which are not available. Evaluation of each term could be made if both s_c and α are known for four 1–1 electrolytes containing all four different ions, since a system of eight equations with eight unknowns could be written from equations (11) and (12). Another method to evaluate these quantities, perhaps more adaptable to experimental application, would be the determination of both s_c and the thermoelectric coefficient at infinite time for four 1–1 electrolytes containing four different ions. A system of eight equations with eight unknowns very similar to the above could be established.[18]

There are not enough data in the literature to perform such calculations. However, it is possible to group the unknowns in equations (11) and (12) in such a way that

$$\begin{aligned} q_D' + q_D'' &= q_D \\ q_A' + q_A'' &= q_A \end{aligned} \qquad (13)$$

where q_D means the net energy that opposes the departure of the anion and cation of the electrolyte, and q_A the energy necessary for the formation of the holes at the new positions where they arrive. From a knowledge of s_c and α for a 1–1 electrolyte q_D and q_A could be determined.

From the data of James and Gordon[11] for 0.100 N HCl at 25°

$$q = q_D + q_A = 4.0 \text{ kcal. per mole}$$

and from equations (11) and (13)

$$q_D - q_A = 2(s_N)RT^2 = 2(3.2)(1.99)(298)^2 \times 10^{-3} = 0.113 \text{ kcal.}$$

from which $q_D = 2.06$ kcal. and $q_A = 1.94$ kcal.

Similar computation for HCl 0.100 N at 35°, for which James and Gordon report $q = 3.8$ kcal., yields $q_D = 1.98$ kcal. and $q_A = 1.82$ kcal.

These values indicate that the energy that opposes the departure of the cation and anion of HCl from their cages is greater, but almost equal to the energy required to open holes at their positions of arrival. It is this small difference, called the heat of transport, which bears directly proportionality to the Soret coefficient. The net heat of transport Q^* for the ions of HCl in 0.100 N solution is found to be 120 cal. at 25° and 160 cal. at 35°.

DURHAM, N. C. RECEIVED FEBRUARY 12, 1951

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

The Photolysis of Acetone: Diffusion of Methyl Radicals from the Light Beam and the Activation Energy of Hydrogen Abstraction

BY A. J. C. NICHOLSON[1]

The photolysis of acetone has been studied over a wide range of temperature, pressure and light intensity. The existing theory of methane and ethane production has been shown to be valid provided the temperature is above 100°, the acetone concentration is above 10^{18} molecules/cc., and the absorbed light intensity is above $10^{12.5}$ quanta/cc./sec. Under these circumstances an activation energy of 9.6 kcal. can be identified as the difference between the activation energy with which the methyl radical abstracts hydrogen from acetone and half the activation energy of the methyl–methyl recombination. Below 100°, the existing theory is inadequate and gives a false low value for this activation energy. The effect of diffusion of radicals out of the light beam, in experiments in which the light beam does not fill the reaction cell, has been investigated. The magnitude of the correction that has to be made for this effect has been established under certain specific geometrical conditions. Although it is in the right direction, this correction is too small to bring the low temperature value of the "activation energy" up to its high temperature value.

For any system containing methyl radicals and a molecule from which they can abstract hydrogen, a function, R, may be defined as the ratio of the rate of formation of methane to the square root of the rate of formation of ethane. Dorfman and Noyes[2] showed that, at constant temperature and pressure, R was independent of the absorbed light intensity for the acetone photolysis under the conditions of their experiments. (These authors expressed this result in a different but equivalent notation.) This independence makes R convenient to measure experimentally and important theoretically because a simple mechanism can be postulated to explain it. Dorfman and Noyes postulated (a) that the *only* methane and ethane producing reactions are

$$CH_3 + CH_3 \longrightarrow C_2H_6 \quad d(C_2H_6)/dt = k_1(CH_3)^2 \quad (1)$$

$$CH_3 + CH_3{\cdot}CO{\cdot}CH_3 \longrightarrow CH_4 + CH_2{\cdot}CO{\cdot}CH_3 \quad d(CH_4)/dt = k_2(CH_3)(A) \quad (2)$$

and (b) that these two reactions are exclusively homogeneous and bimolecular and hence that

$$R/(A) = k_2/k_1^{1/2} \qquad (3)$$

Equation (3) gives the required intensity independence to R, enables absolute values of $k_2/k_1^{1/2}$ to be calculated, and from measurements at different temperatures gives an activation energy that should correspond to $E_2 - 1/2E_1$. It further follows that at constant temperature R should vary linearly with acetone pressure. This prediction has been only partially tested experimentally.

Trotman-Dickenson and Steacie[3] have used this

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(1) (a) Present address: c/o C. S. I. R. O., Fisherman's Bend, Melbourne, Australia; (b) The author's thanks are due to the Drs. Camille and Henry Dreyfus Foundation, Inc., for the award of a post-doctoral fellowship: and to the Office of Naval Research, United States Navy, for support under Contract N6onr-241. Task I. (c) For detailed tables of data order Document 3260 from the American Documentation Institute, 1719 N Street, N. W., Washington 6, D. C., remitting $1.00 for microfilm (images 1 inch high on standard 35 mm. motion picture film) or $1.05 for photocopies (6 × 8 inches) readable without optical aid.

(2) L. M. Dorfman and W. A. Noyes, Jr., *J. Chem. Phys.*, **16**, 557 (1948).

(3) (a) A. F. Trotman-Dickenson and E. W. R. Steacie, *J. Chem. Phys.*, **18**, 1097 (1950), and (b) A. C. S. "Symposium on Anomalies in Reaction Kinetics," Minneapolis, June, 1950, *J. Phys. Coll. Chem.*, **55**, in press (1951). The author is indebted to Mr. Trotman-Dickenson and Dr. Steacie for much helpful discussion on this problem and for information about their results prior to publication.

relationship to obtain a comparative series of activation energies for the abstraction of a hydrogen atom from different compounds. Although their value of $k_2/k_1^{1/2}$ for acetone agreed very reasonably at 120° with that found by Dorfman and Noyes, $E_2 - 1/2E_1$ equalled 9.7 kcal. over the range 120–300°[4] while Dorfman and Noyes found 6.0 kcal. over the range 25–120°. Trotman-Dickenson and Steacie pointed out that a recalculation of the results of Saunders and Taylor[5] gives an activation energy, above 150°, in excellent agreement with their value. It may be added, however, that recalculation of Saunders and Taylor's one point at 100° gives a result in equally good agreement with Dorfman and Noyes. This discrepancy clearly requires investigation as it casts doubt on the whole postulated mechanism.

It will be shown below that this disagreement is experimentally real. It is convenient to summarize the differences in the experimental conditions of the two investigations in Table I.

TABLE I

EXPERIMENTAL CONDITIONS: DORFMAN AND NOYES, AND TROTMAN-DICKENSON AND STEACIE

	Condition	D and N	T-D and S
(a)	Wave length of light, Å.	3130	*ca.* 2537
(b)	Absorbed intensity, quanta/cc./sec. $\times 10^{-11}$	0.7–37	8–280
(c)	Decomposition, %	*ca.* 0.04	*ca.* 5.0
(d)	Temperature, °C.	25–122	120–300
(e)	Pressure, mm.	110–160	25–100
(f)	Ratio light volume/dark volume	0.47	0.72

R will be expressed throughout in molecules$^{1/2}$ cc.$^{-1/2}$ sec.$^{-1/2}$ and it must be emphasized that its absolute value depends on the volume used in calculating it. When the light volume and the cell volume differ considerably the choice of the volume to use is entirely arbitrary. The cell volume is the correct one to use if the methyl radicals are considered to diffuse out into the dark space; the light volume if they are considered to react so rapidly that diffusion can be neglected. Very probably an intermediate value is the correct one and this value may vary in a complicated manner with change of pressure, intensity or temperature. No experimental evidence is available on this point although some guidance can be obtained from the calculations of Hill[6a] and Noyes.[6b] The present research was planned to obtain information on this "diffusion effect" and to determine whether such an effect is large enough to explain the activation energy discrepancy. It was further hoped that equation (3) could be tested over a wider range of conditions.

Experimental

The acetone used, Merck and Co., Inc., reagent grade, was dried with "Drierite" and twice distilled in a 35-plate column in an atmosphere of dry nitrogen. The distillate was further dried with anhydrous copper sulfate and a middle cut taken into the apparatus by bulb to bulb fractionation. This acetone was thoroughly degassed before each run. The photolysis products studied, CO, CH_4 and C_2H_6, were pumped off the residual acetone at −130°. In the early runs, up to No. 32, these gases were analyzed by combustion on a heated platinum wire. In the later runs a method described by Linnell and Noyes[7] was used. The ethane was condensed in a cold finger cooled to −210° by a trap containing liquid nitrogen under continuous pumping. The carbon monoxide and methane could then be completely removed and analyzed over heated copper oxide.[8] The residual ethane was warmed up and its pressure measured in a McLeod gage. The two methods agreed well as can be seen from runs 32, 35 in which the products were divided and (i) and (ii) refer to the two methods. The second method takes less time and does not suffer from the occasional "wild" results to which the first is prone. These "wild" results seemed to be due to the difficulty of condensing out every trace of mercury from the combustion tube. Rates of production of gases are expressed throughout in microns/hour measured in a volume of 694 cc. at 27°. Rates in molecules/cc./sec. are obtained by multiplying these by $6.20 \times 10^{12}/V$, where V is the appropriate volume in cc. Unless otherwise indicated V was 15.7 cc., the volume of the light beam; in experiments marked with an asterisk the whole cell was filled with light and V was then 50.0 cc. The limiting accuracy of any experiment can be judged from the total gas measured since the error in measuring any constituent can be reckoned at about ±0.2 micron. It can be seen that it is difficult to measure R accurately over a wide range of conditions. If the ethane measurement is precise the methane error is large and *vice versa*.

The light source was a Hanovia medium pressure mercury arc, Type S-100, except for 4 runs with a General Electric AH-6 arc. The filter designations in the tables correspond to: F, 25 mm. of 0.0005 M potassium chromate solution, 25 mm. of 0.178 M nickel chloride solution, 10 mm. 0.0245 M potassium biphthalate solution, 3 mm. Corex purple-red glass No. 9863, which gave almost monochromatic 3130 Å. light[9]; P, 1.5 mm. Pyrex which gave, of the light absorbed by acetone, 3130 Å. with a little 3020 and 2967 Å. light; Cl, 55 mm. of chlorine at atmospheric pressure which gave mainly 2537 Å. light; and O, the unfiltered arc. Neutral density filters of coated quartz were also used to reduce intensities. Absorbed intensities were calculated from the rate of carbon monoxide formation assuming a quantum yield of 1 above 120° and using the data of Herr and Noyes[10] for lower temperatures. The light was condensed with a quartz lens and a system of stops arranged to give a parallel beam 1 cm. in diameter. One of the greatest sources of error lay in keeping this beam size reproducible and in accurately measuring its volume. The more the arc departs from a true "point source" the greater is the amount of light that is scattered into the reaction cell by the lens, filters and cell window. This scattered light is difficult to see because of the contrast with the bright central beam. Its presence seems to be the only explanation of the fact that the experimental spread of the results with this 1 cm. beam is about four times that of another series in which the light beam was arranged to fill the cell completely with light. (In this latter case the volume is known accurately.) This large experimental spread is obscured and a spurious reproducibility is obtained if the optical system is left undisturbed between runs (see discussion later). Two quartz cells were used, 20 cm. long, with optically matched plane windows of 2 cm. in diameter. The internal diameters of the cells were 1.8 cm. and 5.8 cm. The optical system could be moved laterally so that the beam could be shifted from cell to cell without altering either the focus or the filters. The cells were surrounded by furnaces consisting of solid bronze blocks that projected 1 cm. beyond the cell ends to minimize cooling on the exposed windows. High temperatures were controlled manually to ±1°. Room temperature runs were made with no control and the spread was ±2°.

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[4] These activation energies would lie about 0.2 kcal. lower if a correction was made for the temperature variation of the pre-exponential factor. This factor varies as $T^{1/4}$ not $T^{1/2}$ as stated by Dorfman and Noyes.

[5] K. W. Saunders and H. A. Taylor, *J. Chem. Phys.*, **9**, 616 (1941).

[6] (a) T. L. Hill, *J. Chem. Phys.*, **17**, 1125 (1949); (b) W. A. Noyes, Jr., A. C. S. "Symposium on Anomalies in Reaction Kinetics," Minneapolis, June, 1950; *J. Phy. Colloid Chem.*, **55**, in press (1951).

[7] R. H. Linnell and W. A. Noyes, Jr., THIS JOURNAL, **73**, 3986 (1951).

[8] W. M. Manning, *ibid.*, **56**, 2589 (1934).

[9] R. E. Hunt and W. Davis, Jr., *ibid.*, **69**, 1415 (1947).

[10] D. S. Herr and W. A. Noyes, Jr., *ibid.*, **62**, 2052 (1940).

Results and Discussion

Intensity Dependence of R/A.—To test equation (3), results from Table II[1c] together with the values of T-D and S and D and N, are plotted in Fig. 1 using, for convenience, a logarithmic intensity scale. The greatest weight must be given to the series at 150°, all at 100 mm. pressure with the light filling the cell, for which the size of the circles gives an estimate of the error (± 0.1 μ on the smallest gas constituent). For this series: (1) Over the whole intensity range from 3–3900 ($\times$ 10^{-11} quanta/cc./sec.), R/A equals 8.89 ± 0.36 ($\times$ 10^{13} cc. $^{1/2}$ molecules $^{-1/2}$ sec.$^{-1/2}$—the error is the mean difference—12 measurements). (2) Over the intensity range from 20–3900, R/A equals 9.11 ± 0.12 (9 measurements). (3) Over the intensity range 3–10 R/A equals 8.23 ± 0.06 (3 measurements). Although the magnitude of the change is only about 4 times the experimental error, this lowering of R/A at the low intensities seems significant; especially since the measurements at 122° show the same effect. The change is not due to a wave-length effect. These results are in reasonable agreement with those of the other two investigations and the spread of the individual measurements is appreciably smaller. Unfortunately it was not experimentally possible to follow the trend in R/A to lower intensities. It may be concluded that R/A is independent of intensity to a very good first approximation.

Volume Effect.—For those runs in which the light beam did not fill the cell, a choice of volumes has to be made in calculating R/A. In Table II[1c] the light volume has been chosen and the results would have to be multiplied by 0.56 to be expressed in terms of the cell volume. Examination of the table shows: (1) The average R/A for the "small beam" results is 4.72×10^{-13} while the average for the comparable "filled cell" results is 3.74×10^{-13}. (2) This grand average exaggerates the difference between the two series. If the early small beam results, runs 2, 3, 20, 23, are compared with the filled cell results, especially at similar intensities, the difference between the two series is hardly observable. The large values of R/A for the small beam all date from the use of a new lamp, run 61 and after, which did not give such a compact light source as the earlier lamp. (3) Runs 62 and 64 were made with the new lamp and a very badly focussed beam; the good agreement between them was only obtained because the light beam was undisturbed between runs. For runs 65 and 66 a smaller stop was used in the lamp housing which gave a better beam and brought the value of R/A down toward the earlier values. (4) Run 67 shows that there is no difference between the two lamps when the cell is filled with light.

If the early runs are considered as the "best," since scattered light can only make R/A too large, it may be concluded that diffusion of radicals from the light beam is not very important under the conditions of these experiments. For this reason the points of T-D and S shown in Fig. 1 have been calculated using the light volume. This increases the values given in their paper by 18% and is probably a slight over-correction.

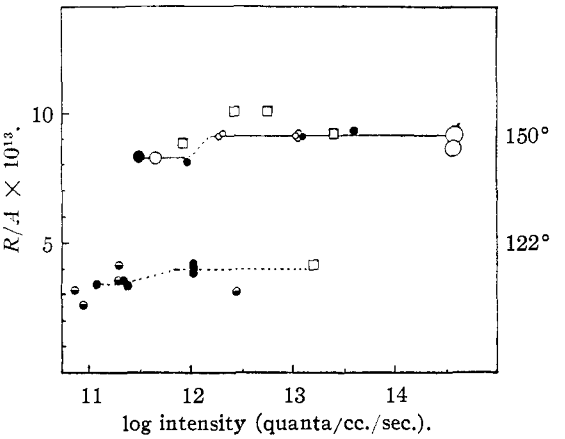

Fig. 1.—Plot of R/A against the logarithm of the absorbed intensity at 122° and 150°: This work, with light filling the cell: ●, at 3130 Å.; ○, with full arc. Small beam calculated on the light volume: ◒, Dorfman and Noyes at 3130 Å.; □, Trotman-Dickenson and Steacie at 2537 Å.

These results are not in agreement with the calculations of Hill[5] who found that diffusion effects should be significant under these conditions. The discrepancy can most probably be explained by Hill's choice of rate constants. For want of experimental evidence, he assumed a steric factor (p) of 2×10^{-2} for the recombination of methyl radicals. Although some earlier work[11,12] indicated a steric factor even lower than that chosen by Hill, Gomer[13] has recently provided evidence that this steric factor is very close to unity. A calculation, for Run 43, of the "root mean square diffusion distance"[5] gives 0.67 cm. using $p = 2 \times 10^{-2}$, and 0.25 cm. using $p = 1$. Since the distance from the beam edge to the walls was 0.4 cm. in these experiments, the choice of rate constants is critical for deciding whether or not diffusion is important.

In Table III[1c] are given results for a 6 cm. diameter cell using a 1 cm. diameter light beam as nearly as possible identical with that used for the experiments in Table II[1c]. Here the values of R/A calculated using the light volume are considerably larger than those found using the 1.8 cm. cell. The surprising result emerges that in a 1.8 cm. cell it appears as if the radicals are effectively concentrated in the light beam, while in a 6 cm. cell, under the same conditions, the radicals appear to have diffused out to give an effective volume considerably larger than the light volume. One explanation of this may be given if it is assumed that methyl radicals are largely reflected from the walls. In the small cell, because of this reflection, the diffusion does not cause a large disturbance in the methyl radical concentration gradient; in the large cell, although relatively few radicals escape from the beam, the fact that even fewer return alters the concentration gradient considerably. Examination of Hill's Fig. 3 shows that the curve of concentration against radius for an infinitely large cell is similar to the curve for a small cell in which every

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(11) R. A. Marcus and E. W. R. Steacie, *Z. Naturforsch*, **4a**, 332 (1949).

(12) D. M. Miller, quoted in ref. 3b.

(13) R. Gomer, *J. Chem. Phys.*, **18**, 998 (1950).

methyl radical striking the wall is captured (does not give either methane or ethane) and markedly different from the curve for the same small cell when complete reflection is assumed.

The opposite situation to that occurring at 122° prevails for runs made at lower temperatures. In Table IV[1c] giving runs at room temperature, the values of R/A are tabulated for both methods of calculation. The experimental spread is large but comparison of Run 13 with Runs 14–19 or 24 with 30 shows that the cell volume values agree better than the light volume values.

Pressure Dependence of R.—Equation (3) requires that, at constant temperature, the plot of R against A should be a straight line through the origin. Such plots are given in Figs. 2 and 3 for 122 and 25°, respectively. Since deviations from a straight line occur it is relevant to consider possible explanations and make quantitative estimates of the deviations they would cause.

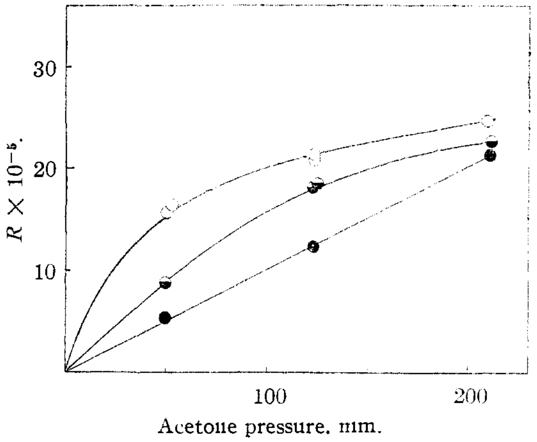

Fig. 2.—Plot of R against A at 122°. Small beam calculated on the light volume: O, 5.8 cm. diameter cell; ◒, 1.8 cm. diameter cell; ●, 1.8 cm. diameter cell filled with light.

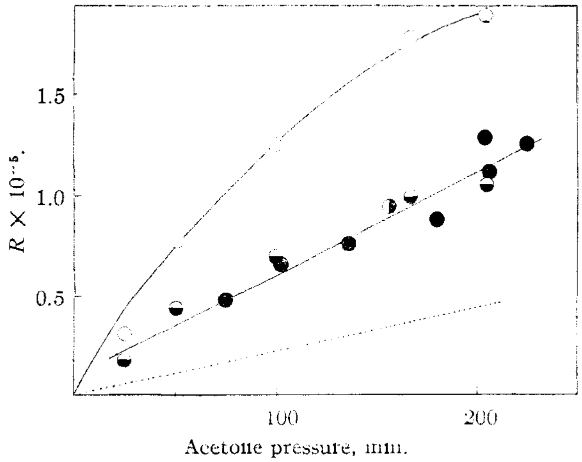

Fig. 3.—Plot of R against A at 26°: O, small beam calculated on light volume; ◒, small beam calculated on cell volume; ●, light filling cell; ◐, Dorfman and Noyes.

(1) Light absorption itself causes a decrease in intensity along the length of the cell. Assuming that the methyl radical concentration in any volume element is twice the local rate of light absorption and that no radicals diffuse out of a volume element, it can be calculated (*cf.* Noyes[6] for an essentially similar calculation for radial diffusion) that

$$R = F\frac{k_2A}{k_1^{1/2}}$$

where

$$F = 1 - e^{-\alpha A l_0}\left(\frac{2}{\alpha A l_0(1 - e^{-2\alpha A l_0})}\right)^{1/2}$$

α = the absorption coefficient and l_0 = the cell length. Luckey and Noyes[14] give $\alpha = 8.47$ at 120° when l_0 is in cm. and A is in moles/liter. Substituting for the highest pressure in Fig. 2 gives a minimum value of F equal to 0.95. This correction can, therefore, be neglected.

(2) In Fig. 2, R has been calculated using the light volume. It is clear from the curves that as the pressure is decreased diffusion of radicals out of the beam causes this volume to be smaller than the "true" volume and hence R to be larger than its "true" value. Unfortunately the curve for the small beam in the small cell is the series, runs 61, 62, 63, with the badly focussed beam so that these values of R are higher than the general average. This effect cannot occur when the cell is filled with light and the plot for the filled cell is, in fact, very nearly a straight line through the origin. A definite decision cannot be made but it is possible that this plot has a small positive intercept. The recalculated results of Saunders and Taylor[5] also give good straight lines and show a trend toward a positive intercept which is larger at 100° than 200°.

In Fig. 3 the values of R have been corrected to 26° by applying a correction of 4% per degree. For the small beam both R (light volume) and R (cell volume) have been plotted and it can be seen that the latter points fit well on to the straight line drawn through the points for the cell filled with light. The point representing the average of Dorfman and Noyes' six points (recalculated using their cell volume) also lies on this line. In spite of the experimental scatter, it seems justifiable to claim that the best line through these points does not pass through the origin. Strictly the slope of this line can no longer be compared with the slopes of lines passing through the origin. However, it may be said that this value of R/A, 1.55×10^{-14}, is the lowest value that can be obtained by correcting for diffusion out of the light beam. Dorfman and Noyes' light volume value of R/A was 2.7×10^{-14}, obtained from an intensity plot at constant pressure. The dotted line is drawn to show where the points would lie if the low temperature activation energy was 9.6 kcal.

(3) The possibility that deviations from linearity are due to the necessity for a third body in the methyl–methyl reaction seems to have been dismissed too cursorily by other workers. Trotman-Dickenson and Steacie[3a] found, at 150°, that R/A increased at very low pressures and their statement "this is in the opposite direction to that which would result from a third body restriction" is not correct. Linnell and Noyes[7] have recently found that even in a cell filled with light, R/A increases below 50 mm. pressure in a way that is consistent with a three-body mechanism. There are two pos-

(14) G. W. Luckey and W. A. Noyes, Jr., *J. Chem. Phys.*, (in press)

sible mechanisms for formation of ethane in a three-body process which give different kinetics according as the short-lived intermediate is taken to be $C_2H_6^*$ (I) or $CH_3 \cdot CH_3COCH_3$ (II). It can be shown that (the full calculation of these results is available on microfilm[1c]): for Mechanism I, (a) R varies as A at high pressure, (b) R varies as $A^{1/2}$ at low pressure, (c) R is always independent of I_a at constant pressure: for Mechanism II, (a) R varies as $A^{1/2}$ $(CH_3)^{1/2}$ at high intensity, (b) R varies as $A^{1/2}$ at low intensity, (c) R is always proportional to $A^{1/2}$ at constant absorbed intensity.

Mechanism I is obviously a much better representation of the experimental observations on both pressure and intensity variation. The possibility that II occurs to a small extent cannot be excluded. The point at which the third body restriction appears in the kinetics is somewhere less than 50 mm. pressure at 150° and this point will occur at even lower pressures at lower temperatures. It may be noted that if, say, 25 mm. is the pressure at which the lifetime of the intermediate is approximately equal to the time between collisions, the lifetime of the $C_2H_6^*$ entity is about 10^{-8} sec. Theoretical calculations of this lifetime have always given a value many powers of ten smaller than this.[15,16,17]

The discussion of the pressure variation may be summarized: Equation (3) is only valid provided the light beam fills the cell, the temperature is higher than 100°, and the acetone concentration is greater than 10^{18} molecules/cc.

Activation Energy of R/A.—In Fig. 4 values of log R/A are plotted against $1/T°$ K. The unmarked straight line is that obtained in this work using the average value, for each temperature, of all experiments with the cell filled with light. The actual points are not given but individual points for the 1 cm. beam are shown and are seen to scatter around the same line. Above 120° agreement with the other works is excellent and within the limitations disclosed by the discussion above, the identification of R/A with $k_2/k_1^{1/2}$ can be considered established. This work then gives $k_2/k_1^{1/2} = 8.21 \times 10^{-8}\ e^{-9600/RT}$ molecules$^{-1/2}$ cc.$^{1/2}$ sec.$^{-1/2}$. At the low temperature, the point represents the value of R/A from the straight line in Fig. 3. It has been shown above that Dorfman and Noyes' low temperature value must be reduced to allow for diffusion out of the beam. It is clear that the maximum correction for this effect is not sufficient to bring the high and the low temperature activation energies into line.

If the differences in technique outlined in Table I are considered, (f) has been discussed above and (b), (c), are clearly unimportant. (a) is also unimportant at high temperatures. The series 14–19 shows that, within a rather wide spread, there is no wave length difference at low temperatures. If anything the 2537 Å. values of R/A are slightly larger than the 3130 Å. values; *i.e.*, the trend is in the wrong direction to explain the activation energy difference. Thus the discrepancy is clearly related to the temperature difference and seems to be associated with a break-down in the pressure relationship at low temperatures.

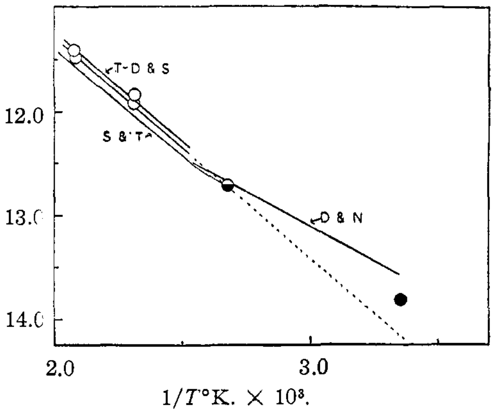

Fig. 4.—Plot of log R/A against $1/T$°K.: straight line for results with the cell filled with light: ○, small beam calculated on the light volume; ●, average of low temperature points calculated on the cell volume; ⊖, Saunders and Taylor.

The most immediate difference in the photolysis at the two temperatures lies in the presence of biacetyl among the low temperature products (and, by inference, of the acetyl radical during the photolysis). It would be expected that if either of these entities took part in a methane or ethane producing reaction, the value of R/A would be more sensitive to wave length than has been found. However, the methyl radical probably abstracts a hydrogen atom very much more easily from biacetyl than from acetone.[6,18] So that it is possible that the presence of biacetyl would cause a lowering of the activation energy of R/A and a departure of the R–A plot from linearity. Alternatively a surface reaction producing methane with a low activation energy or ethane with a high activation energy could be postulated to explain the low temperature results. In the absence of sufficient experimental data, it does not seem profitable to speculate further.

Mean Lifetime Diffusion Distance.—Hill[5] gave a method of calculating a "mean lifetime diffusion distance" and suggested that this distance could be used as a test of whether diffusion is significant under the geometrical conditions of any given photolysis. This distance has been calculated above, in the following manner. Generalizing, perhaps rashly, from Gomer's work,[13] it has been assumed that all the possible radical recombination reactions have steric factors of unity and activation energies of zero. From the experimental values of the rate of ethane formation and of R/A, the methyl radical concentration and k_2 can be calculated and the acetonyl radical concentration, from a steady state equation. From these data, the mean lifetime diffusion distance can be calculated for temperatures above 100° but for lower temperatures so many more assumptions have to be made that the calculation does not seem worth while. The distances obtained by this calculation are reasonable. They are fairly sensitive to the values chosen for the rate constants, especially for k_1, so that this test can

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(15) G. E. Kimball, *J. Chem. Phys.*, **5**, 310 (1937).

(16) L. S. Kassel, *ibid.*, **5**, 922 (1937).

(17) T. L. Hill, *ibid.*, **17**, 503 (1949).

(18) J. G. Roof and F. E. Blacet, THIS JOURNAL, **63**, 1126 (1941), discussed in ref. 6.

only be used as an approximate guide until the magnitudes of the rate constants are more firmly established.

Diffusion Effect: Conclusions.—For the smaller cell used, diffusion of radicals out of the light beam may be neglected provided the temperature is above 100° and the acetone pressure is above 100 mm. There is, however, a small effect present even under these conditions, which becomes more marked the smaller the light beam relative to the cell. In addition surprisingly large errors can be made in determining the volume of a small light beam so that measurements with such beams show a wide experimental spread. At 26°, on the other hand, the radicals diffuse out of the beam to such an extent that it is necessary to use the cell volume in calculations instead of the light volume. For these two reasons it is recommended that measurements should be made with the whole reaction cell filled with light. This involves risking that an unknown surface reaction contributes to the effect being studied: the agreement between different workers makes this risk small in the case of the acetone photolysis.

For photochemical reactions in general the magnitude of the diffusion effect can be calculated by the method given by Hill.[6a] This method requires that all the rate constants involved are known to a fairly high accuracy. Even for acetone the constants are not known well enough for a definite answer to be given; hence it seems that for any less well known reaction only a direct experimental test can decide whether radical diffusion is important or not.

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Photochemical Studies. XLIV. Pyridine and Mixtures of Acetone and Pyridine[1]

By Robert H. Linnell and W. Albert Noyes, Jr.

The rates of formation of methane and of ethane as functions of temperature, volume of light beam, cell length and pressure have been determined for acetone vapor. Pyridine vapor shows little or no decomposition at 2537 A. but does decompose at shorter wave lengths with formation of a brown deposit, hydrogen and C_2 hydrocarbons. Methyl radicals do not abstract hydrogen appreciably from pyridine to form methane under the conditions of these experiments at temperatures from 120 to 210°.

The reactions of methyl radicals to produce methane and ethane during photochemical decomposition of acetone both with and without the addition of foreign gases have been studied by several authors recently.[2] If these two reactions may be written in general terms as

$$CH_3 + CH_3 = C_2H_6; \qquad R_{C_2H_6} = k_1(CH_3)^2 \quad (1)$$

$$CH_3 + RH = CH_4 + R; \qquad R_{CH_4} = k_2(CH_3)(RH) \quad (2)$$

where $R_{C_2H_6}$ and R_{CH_4} are the rates of ethane and of methane formation, respectively, in molecules per cc. per second; it is possible from the slope of a plot of $R_{CH_4}/R_{C_2H_6}^{1/2}$ *vs.* (RH) (where (RH) is concentration in molecules per cc.) to obtain $k_2/k_1^{1/2}$ in (molecules sec.)$^{-1/2}$ cc.$^{1/2}$. This has been done for several different molecules RH by Trotman-Dickenson and Steacie[2b] by assuming that the line goes through the origin.

Gomer,[3] by a rotating sector technique, has obtained recently a value for k_1. If this value is accepted, absolute values of k_2 for several different RH molecules can be obtained from existing data.

Due to the fact that (1) is second order with respect to CH_3 radicals while (2) is first order, and the fact that RH may be any molecule present (including products of acetone photolysis, such as biacetyl), this method of calculation must be examined critically before the reliability of $k_2/k_1^{1/2}$ values can be assessed. Certain aspects of this problem have been discussed,[4] and systematic data bearing on this problem are presented and discussed in the preceding article.[5] The present article contributes certain data of interest, and in addition the reactions of methyl radicals with pyridine are discussed.

The photochemistry of pyridine vapor seems to have received little attention, although the spectrum has been analyzed.[6]

Experimental

The purification of the acetone and the general gas analysis procedure have been described in previous articles.[2a] One modification was introduced since one of the troublesome aspects of earlier procedures was the incomplete separation of ethane from methane and carbon monoxide at the temperature of liquid nitrogen. This was accomplished by using liquid nitrogen cooled to about −215°. Liquid nitrogen was placed between the walls of a cylindrical double-walled vessel which could be connected to an oil-pump. This jacket was placed inside of a standard dewar vessel, and the entire dewar and jacket were filled with liquid nitrogen. Pumping on the nitrogen lowered the temperature to the desired point. The temperature was measured by a thermocouple attached to the outside of the finger in which the gases were condensed. This finger was placed in the inner cylinder of the double-walled vessel. Analyses of known mixtures indicated that carbon monoxide and meth-

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