# PHOTOLYSIS OF DIETHYL KETONE AT LOW PRESSURES: THE PRESSURE DEPENDENCY OF THE COMBINATION OF ETHYL RADICALS[1]

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## ABSTRACT

The photolysis of diethyl ketone has been investigated in the pressure range 0.01–30 mm. at 100°, 150°, 200°, and 250° with a variation in absorbed intensity of 1000-fold. Over this wide variation in experimental conditions the kinetics of the reaction show excellent agreement with the mechanism of Kutschke, Wijnen, and Steacie. Under conditions where the production of ethylene by decomposition of the pentanonyl radical was negligible (high light intensity and low ketone pressure), the ratio of the rate of ethylene formed to the rate of butane produced was determined to be 0.12 independent of the temperature. These data indicate that both the disproportionation and combination of ethyl radicals are homogeneous and pressure independent to as low as 0.01 mm. pressure. In addition it is probable that the two reactions are the result of different reaction intermediates as was postulated by Wijnen and Steacie. The abstraction reaction

$$C_2H_5+C_2H_5COC_2H_5 \rightarrow C_2H_6+C_2H_4COC_2H_5$$

showed definite heterogeneous character at low pressures similar to the analogous reaction of methyl radicals with acetone studied by Ausloos and Steacie.

## INTRODUCTION

The absolute values of the rate constant for the combination of methyl radicals as determined in several independent investigations (2, 5, 10, 11) have differed significantly. Recent papers by Dodd and Steacie (3) and Kistiakowsky and Roberts (7) treat this reaction by a pressure dependent mechanism,

$$2CH_3 \leftrightharpoons C_2H_6^*$$

$$C_2H_6^*+M \rightarrow C_2H_6+M,$$

in an attempt to reconcile these apparent discrepancies. Both studies were made on the photolysis of acetone at low pressures whereby it is possible to compare the rate of ethane formation by combination to the rate of methane formed by the abstraction mechanism,

$$CH_3+CH_3COCH_3 \rightarrow CH_4+CH_2COCH_3.$$

The magnitude of the pressure effects on the relative rates of methane and ethane production can be explained for the most part by such a mechanism, but the lower pressure experiments of Dodd and Steacie indicate other anomalies which are strongly surface dependent. These latter effects have been verified by similar low pressure experiments of Ausloos and Steacie (1).

This paper reports on a similar investigation of the pressure dependency of the combination of ethyl radicals formed in the photolysis of diethyl ketone. It was expected that the experimental difficulties would be somewhat greater than in the acetone photolysis since, presumably, the more complex ethyl

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radicals would not show the effect of third body deactivation for the combination reaction at such high pressures as observed for methyl radicals. On the other hand the disproportionation reaction of ethyl radicals into ethylene and ethane seemed to offer a more reliable comparison reaction than the abstraction reaction which most certainly is partly heterogeneous at low pressures in the case of the acetone photolysis.

## EXPERIMENTAL

The photolysis apparatus was similar to that of Dodd and Steacie (3). A majority of the experiments were conducted in a cylindrical silica cell of 3.9 cm. diameter and 100 cm. length (volume = 1210 cm.$^3$, surface = 1260 cm.$^2$). Another cell of similar dimensions but having two concentrically mounted inner silica tubes (volume = 1040 cm.$^3$, surface = 3580 cm.$^2$) was used in a series of photolyses at 200° in order to evaluate the effect of increased surface and shorter diffusion distance. The method of temperature control of the cells was identical to that used by the above workers. It was possible to maintain the temperature along the cell's length to ±1°. No correction was made for that part of the reaction taking place at the cooler end windows since these cold zones represent a rather small fraction of the total reaction volume.

The light which completely filled the reaction cell in all experiments was a well-collimated beam from a B.T.H. ME/D 250 watt high pressure mercury arc operated on a regulated d-c. supply. A Corning 9-53 filter and the long wave length absorption limit of diethyl ketone limited the absorption region to λλ2800–3200 Å. A plane aluminized mirror was used at the back cell window to increase the light intensity in some of the photolyses and neutral density filters of chromel deposited on silica plates were used to decrease the intensity in other cases.

The per cent decomposition of diethyl ketone was limited in most of the experiments to 0.5 to 4%. However it was necessary to exceed this amount in those photolyses at pressures less than 0.1 mm. pressure and some decompositions were as much as 20%. In all cases the concentration of diethyl ketone used in the various calculations was the average over the run. A supplementary volume of 15 liters was used in conjunction with the photolysis cell in the photolyses under 1 mm. pressure. This additional gas supply was circulated through the reaction cell at frequent intervals during the photolysis by a mercury diffusion pump. Circulation was not carried out during irradiation since the pumping caused considerable pressure differentials within the cell system. Measurement of diethyl ketone pressure was made by a McLeod gauge.

The analytical vacuum system and the diethyl ketone circulation system employed mercury cutoffs throughout, thus eliminating possible errors due to the absorption of diethyl ketone and reaction products in stopcock grease. Photolysis products were separated by use of a Ward–LeRoy still (9) into three fractions: (*a*) CO fraction (volatile at −210°), (*b*) $C_2$ fraction (volatile at −175°), (*c*) $C_4$ fraction (volatile at −115°). These three fractions were analyzed mass spectrometrically. Fraction (*a*) was essentially pure CO. Analysis showed <0.2% $CH_4$ to be present. Fraction (*b*) contained $C_2H_6$, $C_2H_4$, and traces of $C_3H_8$, $C_3H_6$, and $CO_2$. Fraction (*c*) was predominantly $C_4H_{10}$ with small amounts of butene and propene in experiments carried out at high temperature and low intensity.

Eastman Kodak Company diethyl ketone was dried with anhydrous $CaSO_4$ and fractionated in a 15 plate column. Small portions of the fraction boiling from 100.8° to 101.0° (uncorrected) used as a main supply were thoroughly outgassed before each trial in the vacuum system. The perfluorodimethyl cyclohexane obtained from Halogen Chemicals Inc., Columbia, S.C., was distilled and degassed *in vacuo*.

## EXPERIMENTAL RESULTS

In all about 90 runs were made at four different temperatures. The pertinent data for the experiments conducted on diethyl ketone alone are shown in Table I; those shown in Table III refer to the photolyses made in the presence of added perfluorodimethyl cyclohexane, $C_8F_{16}$.

TABLE I

THE RATES OF PRODUCT FORMATION IN THE PHOTOLYSIS OF DIETHYL KETONE

| [D], mole cm.$^{-3}$ × $10^7$ | $R_{CO}$ | $R^{total}_{C_2H_4}$ | $R^{total}_{C_2H_6}$ | $R_{C_4H_{10}}$ |
|---|---|---|---|---|
| | mole cm.$^{-3}$ sec.$^{-1}$ × $10^{13}$ | | | |
| | | 100° | | |
| 0.0320 | 0.840 | 0.0875 | 0.0960 | 0.715 |
| 0.0373 | $1.26^{6}$ | 0.134 | $0.140^{0}$ | $1.09^{3}$ |
| 0.0961 | 2.47 | 0.268 | 0.292 | 2.12 |
| 0.0975 | 3.92 | 0.391 | 0.428 | 3.38 |
| 0.409 | 2.64 | 0.272 | 0.405 | 2.21 |
| 0.468 | 3.00 | 0.282 | 0.475 | 2.53 |
| 0.901 | 2.92 | 0.292 | 0.668 | 2.26 |
| 2.31 | 4.54 | 0.428 | 1.248 | 3.41 |
| 3.69 | 0.744 | 0.0519 | 0.511 | 0.345 |
| 4.29 | $0.169^{0}$ | 0.0123 | $0.178^{8}$ | 0.0415 |
| 4.29 | 0.214 | 0.0122 | 0.201 | 0.0520 |
| 4.29 | 0.772 | 0.0605 | 0.545 | 0.328 |
| 4.46 | 0.861 | 0.0638 | 0.630 | 0.368 |
| 4.67 | $1.62^{5}$ | $0.161^{6}$ | 0.986 | 0.835 |
| 4.29 | 3.48 | 0.307 | $1.56^{0}$ | 2.18 |
| 4.33 | $16.2^{5}$ | $1.53^{4}$ | 4.49 | $11.9^{6}$ |
| 4.29 | 63.2 | 6.25 | $11.9^{7}$ | 51.5 |
| 8.63 | 4.15 | 0.202 | 2.32 | $1.67^{3}$ |
| | | 150° | | |
| 0.00345 | 0.475 | 0.0468 | 0.0633 | 0.385 |
| 0.00412 | 0.587 | 0.0490 | 0.0770 | 0.432 |
| 0.00810 | $1.10^{0}$ | $0.102^{8}$ | 0.129 | 0.908 |
| 0.194 | 2.85 | 0.249 | 0.298 | 2.40 |
| 0.0348 | 3.64 | 0.356 | 0.442 | 3.13 |
| 0.0619 | 6.08 | 0.564 | 0.720 | 5.27 |
| 0.196 | 7.25 | 0.684 | 1.09 | 6.10 |
| 0.353 | 7.18 | 0.665 | 1.41 | 5.78 |
| 0.763 | $1.06^{5}$ | 0.0876 | 0.546 | 0.653 |
| 3.78 | 0.354 | 0.0130 | 0.495 | 0.0352 |
| 3.76 | $1.63^{0}$ | 0.0930 | $1.67^{5}$ | 0.373 |
| 3.76 | 7.10 | 0.486 | 5.05 | 2.99 |
| 3.76 | $12.0^{5}$ | 0.910 | 7.21 | 5.87 |
| 3.71 | 66.1 | 5.56 | 22.7 | 45.1 |
| 3.68 | $199.^{0}$ | 17.6 | 48.9 | $152.^{6}$ |
| 8.27 | 6.08 | 0.292 | 6.65 | $1.37^{5}$ |

TABLE I (*Concluded*)

THE RATES OF PRODUCT FORMATION IN THE PHOTOLYSIS OF DIETHYL KETONE

| [D], mole cm.$^{-3}\times10^{7}$ | $R_{CO}$ | $R^{total}_{C_2H_4}$ | $R^{total}_{C_2H_6}$ | $R_{C_4H_{10}}$ |
|---|---|---|---|---|
| | mole cm.$^{-3}$ sec.$^{-1}\times10^{13}$ | | | |
| | | 200° | | |
| 0.00408 | 0.703 | 0.0655 | 0.0934 | 0.567 |
| 0.00430 | 0.651 | 0.0607 | 0.0955 | 0.556 |
| 0.00425 | 0.575 | 0.0645 | 0.0853 | 0.478 |
| 0.00644 | 0.813 | 0.0795 | $0.116^{4}$ | 0.704 |
| 0.00752 | 0.914 | 0.0914 | $0.131^{5}$ | 0.755 |
| 0.00792 | $1.00^{0}$ | $0.103^{0}$ | $0.149^{5}$ | 0.769 |
| $0.0170^{4}$ | $1.94^{2}$ | $0.186^{0}$ | 0.268 | $1.69^{5}$ |
| $0.0192^{1}$ | $2.12^{0}$ | 0.203 | 0.306 | $1.72^{1}$ |
| 0.0351 | 4.28 | 0.418 | 0.631 | 3.49 |
| $0.165^{8}$ | 8.12 | 0.766 | $1.63^{8}$ | 6.53 |
| 0.341 | 6.14 | 0.553 | 2.03 | 4.25 |
| $1.56^{0}$ | 2.95 | $0.189^{0}$ | 2.98 | 0.707 |
| $1.57^{9}$ | $148.^{8}$ | 45.5 | $12.3^{6}$ | $0.107^{0}$ |
| $1.62^{9}$ | 0.492 | 0.683 | 0.0252 | 0.571 |
| 3.24 | 6.13 | 6.92 | 0.336 | 0.300 |
| 5.40 | 308 | 157.8 | 26.2 | $0.153^{0}$ |
| 5.52 | 2.86 | 4.25 | $0.139^{5}$ | 0.623 |
| 6.84 | 4.03 | 6.11 | 0.143 | 0.382 |
| 8.81 | 0.513 | 0.904 | 0.0244 | 0.960 |
| 9.72 | 0.942 | $1.62^{2}$ | 0.0412 | $1.29^{8}$ |
| $10.1^{4}$ | 43.0 | 49.4 | 2.75 | 0.366 |
| $10.4^{8}$ | 4.71 | 7.33 | 0.220 | 1.04 |
| $11.0^{5}$ | 454 | 311 | 36.1 | 0.184 |
| | | 250° | | |
| 0.00273 | 0.638 | 0.0770 | $0.133^{0}$ | 0.473 |
| 0.00444 | $1.07^{4}$ | $0.118^{5}$ | 0.212 | 0.738 |
| 0.00720 | $1.09^{0}$ | 0.123 | 0.213 | 0.836 |
| 0.00806 | $1.66^{3}$ | $0.181^{6}$ | 0.307 | $1.32^{1}$ |
| $0.169^{3}$ | 2.96 | 0.316 | 0.531 | 2.41 |
| 0.0345 | 5.43 | 0.615 | 1.025 | 4.37 |
| 0.0839 | 9.65 | $1.03^{2}$ | 2.09 | 7.19 |
| 0.278 | 27.1 | 2.70 | 8.67 | $18.6^{5}$ |
| 0.337 | 6.94 | 0.828 | 3.86 | 3.47 |
| 0.708 | 2.92 | 0.479 | 2.82 | 0.605 |
| $1.56^{3}$ | $147.^{3}$ | $12.4^{0}$ | 74.5 | 66.7 |
| $1.61^{5}$ | 8.12 | 0.902 | 9.33 | $1.16^{6}$ |
| 2.85 | 203 | $18.4^{7}$ | $144.^{2}$ | 86.0 |
| 6.43 | 4.87 | 0.598 | 7.70 | 0.0975 |
| 8.68 | $1.81^{5}$ | 0.377 | 2.89 | 0.0240 |
| $10.0^{5}$ | 399 | 32.4 | 422 | 87.2 |
| | | 200° "packed cell" | | |
| $0.0114^{5}$ | 0.456 | 0.0499 | $0.101^{6}$ | 0.402 |
| 0.0352 | $1.60^{4}$ | 0.1675 | 0.332 | $1.29^{4}$ |
| 0.0933 | 4.17 | 0.419 | 0.898 | 3.43 |
| 0.0348 | $15.6^{5}$ | $1.51^{6}$ | 4.17 | $12.3^{0}$ |
| 0.0933 | 40.1 | 3.74 | $14.4^{1}$ | 28.8 |
| 2.35 | 87.2 | 7.53 | 40.6 | 52.5 |
| 4.72 | $154.^{0}$ | $11.3^{0}$ | 85.8 | 82.5 |

## DISCUSSION

### *The Photolysis Mechanism*

Recently a detailed study of the photolysis of diethyl ketone has been made by Kutschke, Wijnen, and Steacie (8). They explained their results on the basis of the following mechanism—

[1] $$C_2H_5COC_2H_5+h\nu \xrightarrow{\phi I_a} 2C_2H_5+CO$$

[2] $$2C_2H_5 \xrightarrow{k_2} C_4H_{10}$$

[3] $$2C_2H_5 \xrightarrow{k_3} C_2H_4+C_2H_6$$

[4] $$C_2H_5+C_2H_5COC_2H_5 \xrightarrow{k_4} C_2H_6+C_2H_4COC_2H_5$$

[5] $$C_2H_5+C_2H_4COC_2H_5 \xrightarrow{k_5} C_4H_9COC_2H_5$$

[6] $$2C_2H_4COC_2H_5 \xrightarrow{k_6} [C_2H_4COC_2H_5]_2$$

[7] $$C_2H_4COC_2H_5 \xrightarrow{k_7} C_2H_4+C_2H_5+CO$$

If the rate of formation of a product, P, is expressed by $R_P$ and the concentration of diethyl ketone by [D] the following expression may be derived.[3]

$$\log(R^{ab}_{C_2H_6}/R_{C_4H_{10}}) = \log(k_4/k_2^{\frac{1}{2}}) + \log([D]/R^{\frac{1}{2}}_{C_4H_{10}})$$

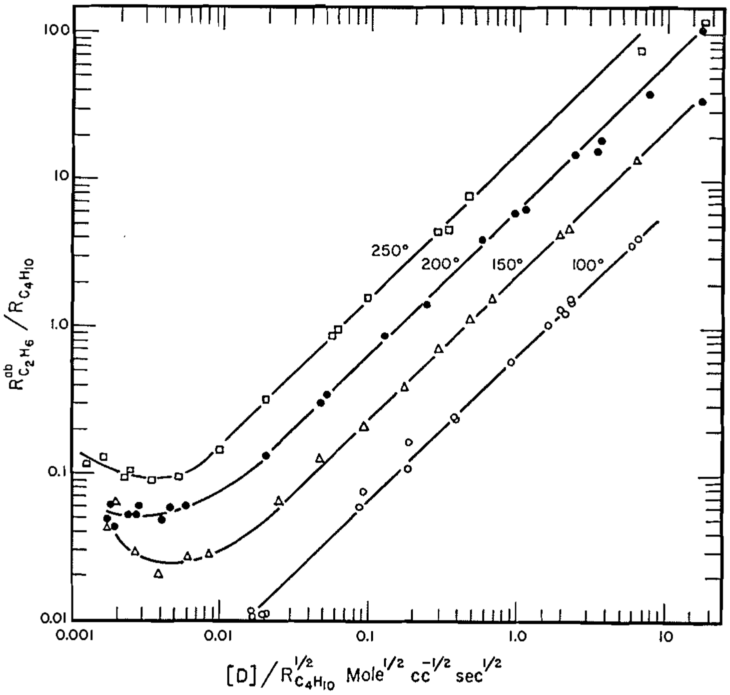

FIG. 1. Plot of $\log R^{ab}_{C_2H_6}/R_{C_4H_{10}}$ vs. $\log [D]/R^{\frac{1}{2}}_{C_4H_{10}}$.

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[3] $R^{ab}_{C_2H_6}$ *represents the rate of ethane formation by the abstraction reaction [4] to differentiate it from* $R^{dp}_{C_2H_6}$, *the rate of ethane formed by the disproportionation reaction [3]. This quantity was calculated from the expression* $R^{ab}_{C_2H_6} = R^{total}_{C_2H_6} - 0.12\ R_{C_4H_{10}}$ *assuming tacitly that the ratio* $k_3/k_2 = 0.12$, *independent of experimental conditions. Justification for this procedure is given in the subsequent discussion.* $R^{ab}_{C_2H_6}$ *is greater than* $\Delta R_{C_2} = R^{total}_{C_2H_6} - R^{total}_{C_2H_4}$, *the rate calculated by Kutschke, Wijnen, and Steacie, by the amount of the additional ethylene produced by the decomposition of the pentanonyl radical,* $C_2H_4COC_2H_5$, *in reaction [7]. In most cases, however, the difference between* $R^{ab}_{C_2H_6}$ *and* $\Delta R_{C_2}$ *is small.*

The results of the present investigation are shown in Fig. 1 as a plot of log $R^{ab}_{C_2H_6}/R_{C_4H_{10}}$ vs. log $[D]/R^{\frac{1}{2}}_{C_4H_{10}}$. Data at the four temperatures cover the pressure range 0.01–30 mm. and represent a variation in absorbed intensity of more than 1000-fold. The series of straight lines of unit slope fit the experimental points well except at the low and high extremes of the variables. Deviations in the low region which occur at pressures under *ca.* 0.4 mm. are treated in detail in a later section; those in the high region are most pronounced at high [D] and low absorbed intensity and are apparent at the two higher temperatures only. A reasonable explanation of these latter anomalies has not been formulated but it is possible that some mode of butane formation in addition to reaction [2] is becoming significant under these conditions. This reaction seemingly must be of the type

$$R + C_2H_5COC_2H_5 \rightarrow C_4H_{10} + \text{other products}$$

where R represents some radical present in the system. Production of detectable amounts of 2-butene and a pentene (2-pentene probably) accompanying the extra amounts of butane could well be the result of the same or a closely related mechanism.

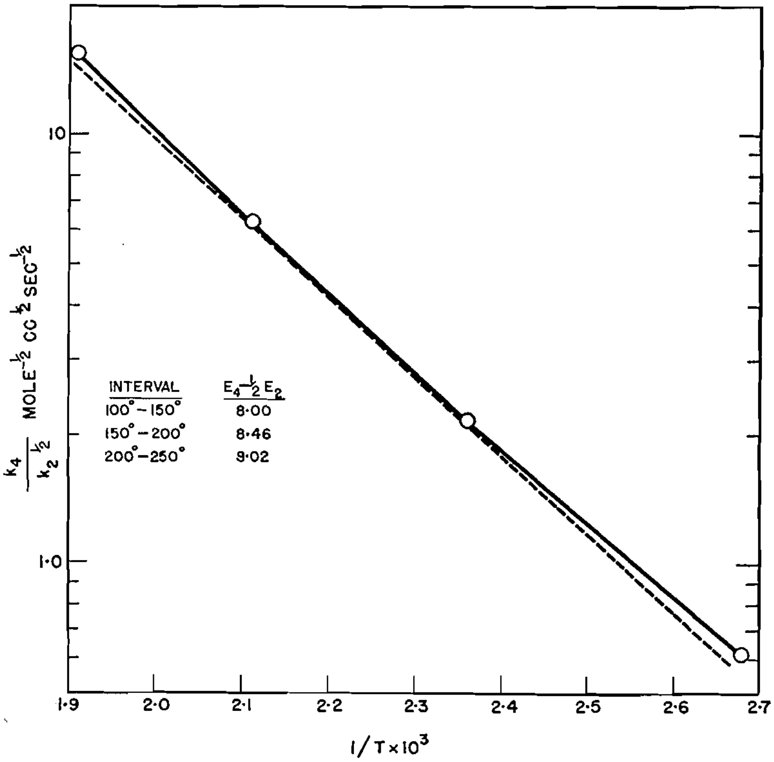

FIG. 2. Arrhenius plot of $k_4/k_2^{\frac{1}{2}}$.

Fig. 2 shows values of log $k_4/k_2^{\frac{1}{2}}$ calculated from the straight line portions of the curves of Fig. 1 plotted vs. $1/T$. The line connecting the four points shows a curvature so the values of $E_4-\frac{1}{2}E_2$ were calculated for each of the three intervals. These activation energies are all higher than the $E_4-\frac{1}{2}E_2 = 7.4$ kcal./mole reported by Kutschke, Wijnen, and Steacie. Reasons for these differences are not altogether clear but it may be pointed out that almost all of their experiments were conducted at ketone pressures greater than 10 mm. In this region it has been indicated that the values of $k_4/k_2^{\frac{1}{2}}$ tend to be too small at higher temperatures, and hence a calculated activation energy would be low in value. The curvature, although not large, seems to be real and is perhaps the consequence of the diethyl ketone molecules having both a primary and secondary hydrogen atom available for the abstraction process. Activation energies of these two processes would be expected to differ by several kcal./mole (13) and lead to a curvature of the type observed.

No attempt was made in the course of the study to analyze for the products of reactions [5] and [6], ethyl butyl ketone and bipentanonyl respectively. However, it is possible to calculate the rate of production of these two substances by a consideration of the balance of the radicals involved,

$$R_{\mathrm{CO}}-R^{\mathrm{p}}_{\mathrm{C_2H_4}} = R_{\mathrm{C_4H_{10}}}+R^{\mathrm{dp}}_{\mathrm{C_2H_4}}+R_{\mathrm{C_2H_5COC_4H_9}}+R_{\mathrm{(C_2H_4COC_2H_5)_2}}$$

(total radical balance)

$$R^{\mathrm{ab}}_{\mathrm{C_2H_6}} = R_{\mathrm{C_2H_5COC_4H_9}}+2R_{\mathrm{(C_2H_4COC_2H_5)_2}}+R^{\mathrm{p}}_{\mathrm{C_2H_4}}$$

(pentanonyl radical balance).

Then

$$\frac{R_{\mathrm{C_2H_5COC_4H_9}}\,[\mathrm{D}]}{R^{\frac{1}{2}}_{\mathrm{(C_2H_4COC_2H_5)_2}}\,R^{\mathrm{ab}}_{\mathrm{C_2H_6}}} = \frac{k_5}{k_6^{\frac{1}{2}}k_4} \text{ and } \frac{R_{\mathrm{C_2H_5COC_4H_9}}}{R^{\frac{1}{2}}_{\mathrm{(C_2H_4COC_2H_5)_2}}\,R^{\frac{1}{2}}_{\mathrm{C_4H_{10}}}} = \frac{k_5}{k_6^{\frac{1}{2}}k_2^{\frac{1}{2}}}.$$

Ratios of rates shown in the latter two equations have been calculated for those experiments at the three higher temperatures in which the amount of ethylene formed by reaction [7] was large enough to justify such a procedure. These ratios shown in the second and third columns of Table II have a good precision at each temperature considering the indirect nature of the calculations involved. In addition $E_4-E_5+\frac{1}{2}E_6 = 7.1$ kcal./mole estimated from the second column ratios compares well with $E_4-\frac{1}{2}E_2 \backsim 8.0$ kcal./mole determined directly while $E_5-\frac{1}{2}E_6-\frac{1}{2}E_2$ from the third column data is about zero.

TABLE II

MECHANISM VALIDITY OF THE DIETHYL KETONE PHOTOLYSIS

| | $k_5/k_6^{\frac{1}{2}}k_4$, mole$^{\frac{1}{2}}$ cm.$^{-3/2}$ sec$^{\frac{1}{2}}$. | $k_5/k_6^{\frac{1}{2}}k_2^{\frac{1}{2}}$ |
|---|---|---|
| 150° (6 runs) | $0.666\pm0.136$ | $1.50\pm0.30$ |
| 200° (10 runs) | $0.311\pm0.061$ | $1.61\pm0.35$ |
| 250° (4 runs) | $0.135\pm0.029$ | $1.92\pm0.35$ |
| | $E_4-E_5+\frac{1}{2}E_6 = 7.1$ kcal./mole | |
| | $E_5-\frac{1}{2}E_6-\frac{1}{2}E_2 \sim 1$ kcal./mole | |

Since $E_2$, $E_5$, and $E_6$ are activation energies of radical–radical combination reactions and are probably near zero, the agreement of the calculated values with those predicted by analogy to other similar mechanisms is excellent. The above treatment gives strong evidence that only the seven reactions enumerated by Kutschke, Wijnen, and Steacie are required to describe the photolysis of diethyl ketone adequately in the temperature range 150°–250°. The actual magnitude of the derived quantities must be accepted with some reservation because of the type of operations necessary in making the calculations.

*The Formation of Ethylene*

The ratio $R^{\text{total}}_{\text{C}_2\text{H}_4}/R_{\text{C}_4\text{H}_{10}}$ at temperatures under 150° was shown by Kutschke, Wijnen, and Steacie to be about constant at $\backsim 0.1$. However, at higher temperatures, and especially at high diethyl ketone concentrations and low absorbed intensities, this ratio increased. It was this latter evidence that led them to add reaction [7] to the mechanism of Dorfman and Sheldon (4). In the present study the absorbed intensity and ketone concentration have been varied over a much wider range and the essentials of this study are shown in Fig. 3 where $R^{\text{total}}_{\text{C}_2\text{H}_4}/R_{\text{C}_4\text{H}_{10}}$ is plotted vs. $R_{\text{CO}}$.[4] It is evident that $R^{\text{total}}_{\text{C}_2\text{H}_4}/R_{\text{C}_4\text{H}_{10}}$ tends toward a constant value of about 0.11–0.12 as the absorbed intensity is

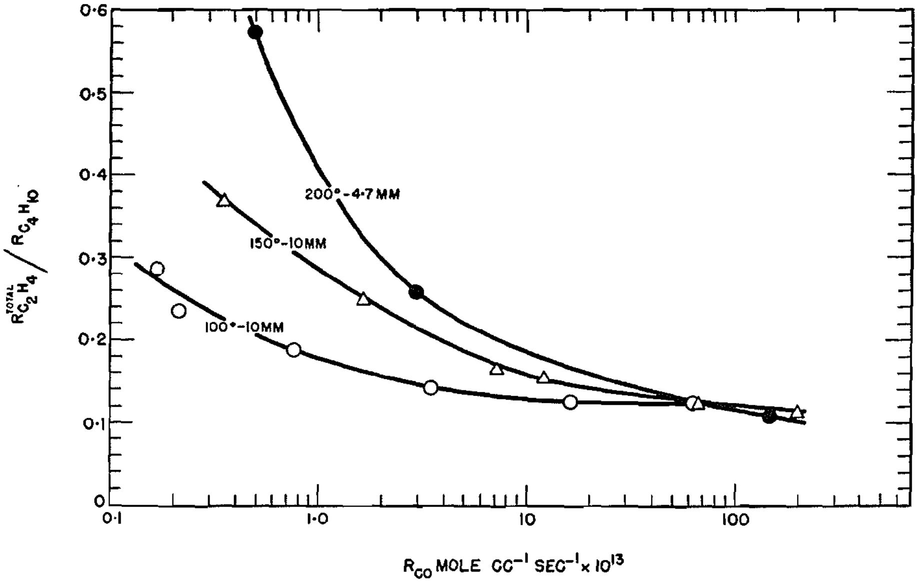

FIG. 3. Plot of $R^{\text{total}}_{\text{C}_2\text{H}_4}/R\text{C}_4\text{H}_{10}$ vs. $R_{\text{CO}}$.

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[4] *The quantum yield of diethyl ketone was carefully determined by Dorfman and Sheldon (4) at 60° and 120°. They found $\Phi_{\text{CO}}$ = 1.0 within experimental error and consequently wrote reaction [1] as given previously. Thus it would seem that even at 60° any propionyl radical formed by* $C_2H_5COC_2H_5 \xrightarrow{h\nu} C_2H_5 + C_2H_5CO$ *would decompose before appreciable participation in other reactions causing its disappearance. At higher temperatures reactions [4] and [7] constitute a chain mechanism for CO production. However, a calculation from the data of Table I shows that no more than ca. 13% of the total CO is formed by reaction [7] in even the most unfavorable case at 250°. For this reason* $R_{\text{CO}}$ *may be taken as a good approximation of the absorbed intensity.*

increased. For a given intensity the deviation from this value is greater at higher temperatures, and, although not indicated in Fig. 3, for fixed temperature and intensity a higher pressure is accompanied by greater deviations. The values of relatively few of the ratios are shown in Fig. 3 but those of all the photolyses follow the generalizations just given in a very regular manner as may be verified by simple calculations from Table I. At 250° the ratio was never lower than about 0.13 even in the very low pressure region. In fact at constant maximum *incident* intensity the minimum of 0.131 was at $[D] = 0.0345 \times 10^{-7}$ mole cm.$^{-3}$; both higher and lower concentrations produced a larger ratio. It is probable that the lower absorbed intensities due to the smaller percentage absorption at the concentrations below $[D] = 0.0345 \times 10^{-7}$ more than offset the effects of the lower concentrations of diethyl ketone tending to decrease the value of $R^{\text{total}}_{C_2H_4}/R_{C_4H_{10}}$. Limits on the intensity imposed by the B.T.H. lamp prevented a real test of this latter explanation.

The evidence given in the preceding sections indicates rather clearly that the disproportionation of ethyl radicals in the photolysis of diethyl ketone in the 3000 Å region is essentially independent of experimental conditions of temperature, intensity, and pressure over a very wide range. The variation in $R^{\text{total}}_{C_2H_4}/R_{C_4H_{10}}$ seems well explained by the production of extra ethylene formed by pentanonyl radical decomposition, reaction [7]. Calculation of $R^{\text{dp}}_{C_2H_4} = 0.12\, R_{C_4H_{10}}$ made earlier in the paper is justified on the basis of such a mechanism. The apparent value of the disproportionation to combination for other systems, especially in the photolysis of diethyl mercury, differs markedly from this value. Discussions of these other determinations are given by Ivin, Wijnen, and Steacie (6) and LeRoy and co-workers (12), and it appears that all recent evidence is in agreement with $k_3/k_2 = 0.12$–$0.15$.

### *The Combination of Ethyl Radicals. Third Body Effects*

The influence of a third body effect on the combination of ethyl radicals in the photolysis process is conveniently demonstrated by comparing the rate of the combination reaction to the rate of some other reaction occurring simultaneously. This comparison reaction must not be dependent on such a third body deactivation. Both Dodd and Steacie (3) and Kistiakowsky and Roberts (7) used the methyl radical abstraction of a hydrogen atom from acetone for this purpose. An analogous treatment in the case of the diethyl ketone photolysis leads to the equations,

$$2C_2H_5 \xrightarrow{k_a} C_4H_{10}^*$$

$$C_4H_{10}^* \xrightarrow{k_b} 2C_2H_5$$

$$M + C_4H_{10}^* \xrightarrow{k_c} C_4H_{10} + M$$

$$R_{C_4H_{10}} = \frac{k_a[M]}{k_b/k_c + [M]}[C_2H_5]^2 \qquad [M] \gg k_b/k_c, \quad R_{C_4H_{10}} = k_a[C_2H_5]^2;$$

$$[M] \ll k_b/k_c, \quad R_{C_4H_{10}} = \frac{k_a k_c}{k_b}[M][C_2H_5]^2.$$

Thus if [M] is limited to diethyl ketone as a third body, the formation of butane should be independent of [D] above some low pressure. By using the rate of ethane formation by the abstraction reaction [4], $R^{\mathrm{ab}}_{\mathrm{C_2H_6}} = k_4[\mathrm{C_2H_5}][\mathrm{D}]$, as a measure of the ethyl radical concentration, equations [I] and [II],

$$\frac{R^{\mathrm{ab}}_{\mathrm{C_2H_6}}}{R^{\frac{1}{2}}_{\mathrm{C_4H_{10}}}[\mathrm{D}]} = \frac{k_4}{k_a^{\frac{1}{2}}}\left[1+\frac{k_b}{k_c[\mathrm{D}]}\right]^{\frac{1}{2}}, \qquad [\mathrm{I}]$$

$$\frac{R^{\mathrm{ab}}_{\mathrm{C_2H_6}}}{R^{\frac{1}{2}}_{\mathrm{C_4H_{10}}}[\mathrm{D}]^{\frac{1}{2}}} = \frac{k_4}{k_a^{\frac{1}{2}}}\left[\frac{k_b}{k_c}+[\mathrm{D}]\right]^{\frac{1}{2}}, \qquad [\mathrm{II}]$$

may be derived. At a single temperature the first of these expressions should approach a constant value with increasing [D] while the latter should tend toward constancy at low [D] values. These two functions are plotted vs. [D] in Figs. 4 and 5. The curves of Fig. 4 follow in a general way the predicted trend except for the experiments at the highest pressures in which the absorbed intensity was low. A possible explanation of this deviation has been given previously. The curves of Fig. 5 all show a decided increase in the low pressure region where they should be essentially constant if they were to behave as predicted by equation [II]. The dotted curve of Fig. 5 indicates that the data obtained at 200° in the cell with the increased surface area deviate to a still greater extent. It is evident that some heterogeneous reaction is affecting the variables of equations [I] and [II] in the low pressure region. How much of the total defect in the low pressure values of equation [I] from the high pressure value of $R^{\mathrm{ab}}_{\mathrm{C_2H_6}}/R^{\frac{1}{2}}_{\mathrm{C_4H_{10}}}[\mathrm{D}]$ is due to surface effects and how much is due to a third body deactivation anomaly is difficult to assess by this treatment. It seems significant that the minima in the curves of Fig. 5 occur at lower pressures (*ca.* 0.1 mm.) than do the corresponding ones (0.5–2 mm.) for the photo-

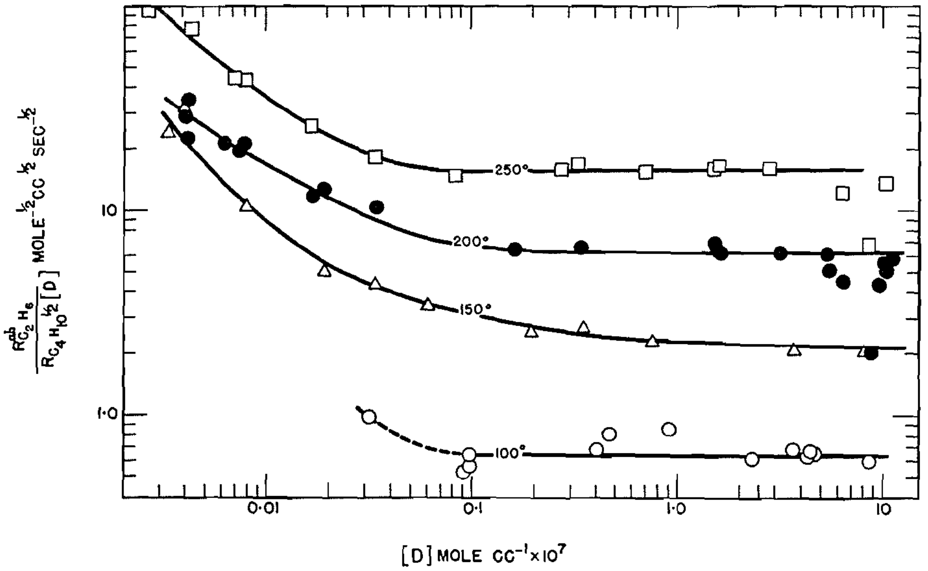


FIG. 4. Plot of $R^{\mathrm{ab}}_{\mathrm{C_2H_6}}/R^{\frac{1}{2}}_{\mathrm{C_4H_{10}}}[\mathrm{D}]$ vs. [D].

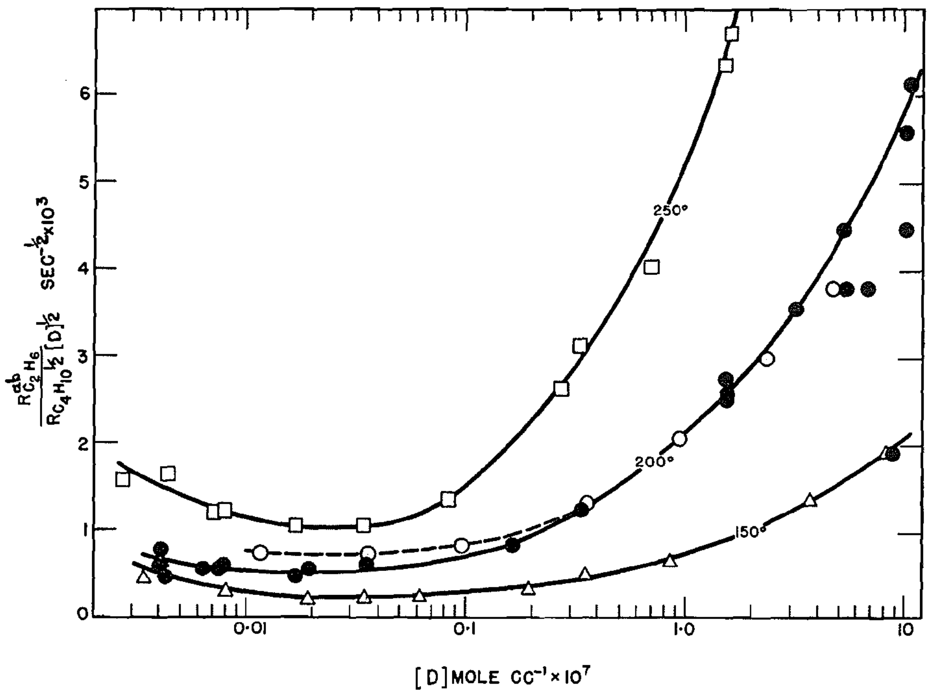


FIG. 5. Plot of $R^{ab}_{C_2H_6}/R^{\frac{1}{2}}_{C_4H_{10}}[D]^{\frac{1}{2}}$ vs. [D].

lysis of acetone given by Ausloos and Steacie (1). Since the influence of a heterogeneous reaction should not be appreciably different for the two ketones, the minima at lower pressures in the case of diethyl ketone could well indicate a much smaller third body effect.

A less complex and seemingly more meaningful treatment of the third body effect in the case of diethyl ketone is to compare the rate of disproportionation to the rate of combination. Although the reactants are identical in the two reactions it will be assumed that the two reaction intermediates differ and that the complex for the disproportionation reaction is not influenced by a third body effect. The disproportionation scheme will be

$$2C_2H_5 \xrightarrow{k_\alpha} C_4H_{10}^{**}$$

$$C_4H_{10}^{**} \xrightarrow{k_\beta} 2C_2H_5 \qquad R^{dp}_{C_2H_4} = [k_\alpha k_\gamma/(k_\beta+k_\gamma)]\,[C_2H_5]^2$$

$$C_4H_{10}^{**} \xrightarrow{k_\gamma} C_2H_4+C_2H_6$$

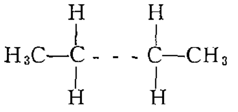
If this latter rate is combined with the expression already derived for the third body mechanism for butane formation, the rate of disproportionation to combination becomes

$$\frac{R^{dp}_{C_2H_4}}{R_{C_4H_{10}}} = \frac{k_\alpha k_\gamma/(k_\beta+k_\gamma)}{k_a k_c[D]/(k_b+k_c[D])}\,.$$

Since it has been found that this ratio is 0.12 independent of experimental conditions, it must be true that $[M]k_c \gg k_b$ or that the combination reaction is not showing a dependency on a third body deactivation down to pressures as low as 0.01 mm.

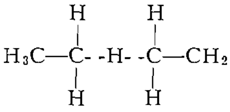
It is necessary to substantiate the two postulates made in the previous discussion: (*a*) the reaction intermediates of the disproportionation and combination reactions differ, and (*b*) the disproportionation complex will not be third body dependent. The two complexes may be represented as

$C_4H_{10}^*$



$$H_3C-\underset{H}{\overset{H}{C}}\cdots\underset{H}{\overset{H}{C}}-CH_3$$

$C_4H_{10}^{**}$



$$H_3C-\underset{H}{\overset{H}{C}}\cdots H\cdots\underset{H}{\overset{H}{C}}-CH_2$$

These same complexes were postulated by Wijnen and Steacie (14) to explain the composition of the various deuterated ethylenes formed in the photolysis of 2,2′4,4′ tetradeuterodiethyl ketone. Their evidence strongly supports a "head to head" intermediate for the combination and a "head to toe" intermediate for the disproportionation.

A consideration of the possible fates of the two complexes and the energetics involved leads to the conclusion that they should have very different response to a collisional deactivation. The combination of two ethyl radicals to form $C_4H_{10}^*$ produces a molecule essentially of the butane configuration which is "hot" by about 80 kcal./mole compared to the final butane product. If the possibilities of H atom rearrangements are ruled out as seems to be the case from Wijnen and Steacie's results (14), the only possible reactions available for $C_4H_{10}^*$ are deactivation by collision and dissociation into the original ethyl radicals. The $C_4H_{10}^{**}$ complex, on the other hand, cannot be deactivated to a stable molecule without an H atom shift. In addition the complex is not as "hot" as is $C_4H_{10}^*$ when it is compared to its end products, $C_2H_4$ and $C_2H_6$ ($2C_2H_5 \rightarrow C_2H_4+C_2H_6$, $\Delta H = -59$ kcal./mole). Most important, however, is the ability of the two product fragments of almost equal mass to distribute this excess energy between them so that the 30 kcal./mole carried by each product is far below that necessary to decompose either the ethylene or ethane.

A further test of the role of a third body was attempted by adding perfluorodimethyl cyclohexane to the reaction system. This gas was chosen because (*a*) its physical characteristics allowed an easy separation from the products of the photolysis, (*b*) it was transparent to the radiation used in the photolysis, (*c*) it was inert to the various radicals formed in the photolysis, and (*d*) the data of Dodd and Steacie indicated that its efficiency as a third body was quite high. Runs were made at 200° and 250° using essentially constant intensity and ketone concentration but with varying amounts of $C_8F_{16}$ added. Experimental data and various calculated parameters for these runs are given in Table III. The most significant and unexpected result of the experiments was the increase in $R^{\text{total}}_{C_2H_4}/R_{C_4H_{10}}$ with an increase in $C_8F_{16}$ concentration. Inas-

TABLE III

THE EFFECT OF ADDED PERFLUORODIMETHYL CYCLOHEXANE, $C_8F_{16}$

| [D] (mm.) | $C_8F_{16}$ (mm.) | $R_{CO}$ | $R^{total}_{C_2H_4}$ | $R_{C_4H_{10}}$ | $R^{ab}_{C_2H_6}$ | $\frac{R^{total}_{C_2H_4}}{R_{C_4H_{10}}}$ | $\frac{R^{ab}_{C_2H_6}}{R^{\frac{1}{2}}_{C_4H_{10}}[D]}$ |
|---|---|---|---|---|---|---|---|
| | | mole cm.$^{-3}$ sec.$^{-1}\times10^{13}$ | | | | | |
| | | | 200° | | | | |
| 0.0234 | 0 | 1.00 | $0.103^{0}$ | 0.769 | .0535 | 0.134 | 24.4 |
| 0.0234 | 0.552 | 0.958 | $0.106^{6}$ | 0.783 | .0404 | 0.136 | 18.2 |
| 0.0215 | 1.60 | 0.933 | $0.107^{8}$ | 0.746 | .0367 | 0.144 | 17.9 |
| 0.0235 | 4.95 | 0.971 | $0.127^{5}$ | 0.710 | .0389 | 0.180 | 20.8 |
| | | | 250° | | | | |
| 0.0236 | 0 | $1.09^{0}$ | 0.123 | 0.836 | .108 | 0.147 | 53.3 |
| 0.0246 | $0.177^{2}$ | $1.18^{8}$ | 0.127 | 0.874 | .107 | 0.145 | 48.1 |
| 0.0248 | $1.16^{2}$ | $1.19^{5}$ | 0.162 | 0.794 | .149 | 0.204 | 72.0 |
| 0.0238 | 4.99 | $1.19^{6}$ | 0.169 | 0.767 | .120 | 0.220 | 59.4 |

much as the formation of butane would not be expected to be made less favorable by an added gas, the increase in the ratio must be attributed to an enhanced $C_2H_4$ formation. It seems likely that the unimolecular pentanonyl radical decomposition, reaction [7], is in its pressure dependent region at 0.02 mm. of diethyl ketone. Addition of $C_8F_{16}$ must aid in the deactivation of the pentanonyl reaction complex thus increasing the $C_2H_4$ formation.

Values of $R^{ab}_{C_2H_6}/R^{\frac{1}{2}}_{C_4H_{10}}[D]$ in the last column of Table III, although not constant to a high degree of precision, show no trend with increasing $C_8F_{16}$ concentration. The poorer agreement between the values is compatible with the difficulty of analyzing for the photolysis products contained in the very large amounts of added $C_8F_{16}$. The lack of any appreciable effect of even high $C_8F_{16}$ concentrations on $R^{ab}_{C_2H_6}/R^{\frac{1}{2}}_{C_4H_{10}}[D]$ may substantiate the independence of the ethyl radical combination to pressure. Unfortunately this latter evidence is complicated by the unevaluated effect of the added gas on the heterogeneous formation of ethane. It might be expected that the greater gas concentration would reduce the rate of radical diffusion to the wall and in addition perhaps reduce the concentration of adsorbed substrate. Since both these effects would tend to decrease the heterogeneous ethane formation it is surprising that the values in the last column of Table III do not decrease at the high $C_8F_{16}$ concentrations.

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