[Joint Contribution from the National Research Council of Canada and the Department of Chemistry, University of Rochester]

Mechanism of the Photolysis of Diethyl Ketone

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The photolysis of diethyl ketone has been investigated over the temperature range 25 to 300° at various pressures and intensities. The formation of butane, ethane and ethylene may be accounted for by reactions (2), (3), (4) and (7) the last reaction becoming more important at higher temperature and/or low intensity. Activation energy differences are found as follows: $E_4 - {}^1/{}_2E_2 = 7.4$ kcal./mole; $E_3 - E_2 = 0$ kcal./mole.

Introduction

The photolysis of diethyl ketone has been the subject of several recent publications.[2,3] This paper reports the results of two independent investigations of the photolysis, many of the results of which were so similar that joint publication was deemed desirable.

The ketones have been shown to be admirable sources of radicals for the study of abstraction reactions with compounds containing hydrogen; a rigorous study of such reactions, however, requires a very complete knowledge of the photodecomposition of the substrate. It was felt that previous work had only incompletely covered diethyl ketone especially in the range of higher temperatures and intensities.

Experimental

In both investigations conventional high vacuum technique has been employed although construction and analytical methods differed somewhat in details.

National Research Council: The storage vessel containing diethyl ketone was separated from the reaction cell by a mercury cut-off. The cylindrical quartz reaction cell was 10-cm. long (volume 195 cc.) and had fused quartz windows. A mercury cut-off separated the reaction cell from the analysis system containing one trap, two modified Ward stills,[4] a Toepler pump and gas buret.

CO, C_2H_6 and C_2H_4 were removed together at −170°; after measuring the total pressure, the CO was determined in a Blacet–Leighton apparatus by absorption on silver oxide,[5] and C_2H_4 by absorption on mercuric acetate.[6] The difference between the total pressure and the sum of the partial pressures of CO and C_2H_4 gave the amount of C_2H_6.

The C_4H_{10} fraction was removed at −115° and measured in the gas buret.

The temperature of the aluminum block furnace containing the reaction vessel was measured by means of a copper-constantan thermocouple and controlled to ±0.5° with a photoelectric relay operating on the light beam from the potentiometer galvanometer.

The light source was a Hanovia S500 medium pressure mercury arc. The beam was collimated by stops and two lenses and formed an illuminated volume of 100 cc. in the cell. The light intensity was varied by the use of drilled plates and by neutral density filters of chromel deposited on quartz. In a few preliminary runs a chlorine filter and a Corning No. 9863 filter were used; the results were the same as those obtained with unfiltered light of the same intensity. Therefore, no filters for monochromatic illumination were employed.

The diethyl ketone used in these experiments was obtained from the Eastman Kodak Company and was distilled once *in vacuo* before use.

Rochester: Eastman Kodak Company diethyl ketone was distilled under dry Linde nitrogen through *ca.* 30 theoretical plates. A constant boiling middle third (102.7° corrected; lit.,[7] 102.7°) was thoroughly outgassed in the vacuum line and stored behind a mercury cut-off; small samples were further outgassed for use in each run. Ketone pressures were adjusted to yield constant concentration at the various temperatures employed.

The fused quartz reaction cell was 20-cm. long and had a cylindrical volume of 76 cc. It was housed in an aluminum block furnace manually controlled during a run to within ±0.5°.

A General Electric AH-6 high pressure mercury arc (illuminated volume 76 cc.) and a Hanovia S100 Alpine Burner (illuminated volume 57 cc. except for a few runs at 56° in which the light beam filled the cell) were used as light sources; after collimation by a single quartz lens, the effective radiation was limited to λλ 2900–3200 Å. by the transparency of the ketone to longer wave lengths,[8] and by the use of a Pyrex filter. Intensity was varied by neutral density filters (chrome aluminum alloy on quartz).

CO and C_2 hydrocarbons were removed from the higher boiling constituents at −155°; combustion data showed that no C_4 hydrocarbons were present. After a measurement of the total pressure the C_2 hydrocarbons were condensed at −215°, using a pumped-down liquid nitrogen trap, and the volatile gas measured. In some experiments this volatile gas was oxidized over hot copper oxide and found to be only CO (±0.5%); usually the gas was discarded directly to the high vacuum exhaust. A measurement of the C_2 pressure gave a second determination of CO; the direct measurement agreed with that obtained by difference within 0.5%. Unsaturates were determined in the C_2 fraction by the hydrogenation scheme of Moore and Taylor,[9] suitably modified in construction for the use of considerably smaller gas samples.

C_4 hydrocarbons were removed at −115°; combustion data showed that this fraction was uncontaminated with compounds of a carbon number greater than four. In both investigations CH_4, H_2 and C_3 hydrocarbons were shown to be absent under the conditions used.

Table I contains the results of a determination done at

Table I

The Effect of Temperature on the Quantum Yield of CO Formation

Temp., °C.	Press., mm.	I_{abs}, quanta/sec. cm.³ × 10¹³	ϕ_{CO}
25	17.6	1.3	0.60
26	24.8	1.61	.64
50	13.1	0.93	.80
50	19.0	1.19	.85
102	14.3	0.93	.93
176	16.5	1.13	.97
176	17.9	1.20	.99
236	13.3	0.87	1.02
292	15.6	1.05	1.27

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[2] L. M. Dorfman and Z. D. Sheldon, *J. Chem. Phys.*, **17**, 511 (1949).

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[5] F. E. Blacet, G. D. MacDonald and P. A. Leighton, *Ind. Eng. Chem., Anal. Ed.*, **5**, 272 (1933).

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Natl. Res. Council, of the quantum yield of CO production at several temperatures. A convenient actinometer is formed by CO production from acetone, which, at 175° and at pressures greater than 6 cm., is generally accepted to have a unit quantum yield even at the relatively high intensities of this investigation.[2]

Results[10] and Discussion

The following reactions have been proposed by Dorfman and Sheldon.[2]

$$C_2H_5COC_2H_5 + h\nu = 2C_2H_5 + CO \quad (1)$$
$$C_2H_5 + C_2H_5 = C_4H_{10} \quad (2)$$
$$C_2H_5 + C_2H_5 = C_2H_6 + C_2H_4 \quad (3)$$
$$C_2H_5 + C_2H_5COC_2H_5 = C_2H_6 + C_2H_4COC_2H_5 \quad (4)$$

The pentanonyl radical produced in (4) was assumed without direct proof to disappear in a manner analogous to the disappearance of acetonyl in the photolysis of acetone, *viz.*

$$C_2H_5 + C_2H_4COC_2H_5 = C_4H_9COC_2H_5 \quad (5)$$
$$2C_2H_4COC_2H_5 = (C_2H_4COC_2H_5)_2 \quad (6)$$

If C_2 hydrocarbons and butane are produced only by reactions (2), (3) and (4), the following relationships exist

$$\Delta R_{C_2}/R_{C_4} = k_4/k_2^{1/2} \times (D)/R_{C_4}^{1/2} \quad (I)$$
$$R_{C_2}/R_{C_4} = 2k_3/k_2 + k_4/k_2^{1/2} \times (D)/R_{C_4}^{1/2} \quad (II)$$
$$R_{C_2H_4}/R_{C_4} = k_3/k_2 \quad (III)$$

In these expressions (D) represents the concentration of diethyl ketone in molecules/cc. The symbol R_X indicates the rate of production of the product X in molecules/sec./cc. of illuminated volume: $\Delta R_{C_2} = R_{C_2H_6} - R_{C_2H_4}$ and $R_{C_2} = R_{C_2H_6} + R_{C_2H_4}$. The determination of $k_4/k_2^{1/2}$ and k_3/k_2 may be carried out in two essentially similar ways, but employing different methods of treating the data. In the first of these methods, $\Delta R_{C_2}/R_{C_4}$ and R_{C_2}/R_{C_4} are plotted against $(D)/R_{C_4}^{1/2}$ at constant temperature; the slopes of both straight lines should be identical and equal to $k_4/k_2^{1/2}$ while the intercept of the latter plot is determined by k_3/k_2. Different values of the variables may be obtained by varying I_{abs} at constant concentration, concentration at constant I_{abs}, or pressure at constant incident intensity (I_0), which essentially varies both concentration and I_{abs} simultaneously. Repetitions at a number of temperatures yield data for the determination of activation energy differences. Dorfman and Sheldon[2] employed this method but were unable to plot $\Delta R_{C_2}/R_{C_4}$ since they did not analyze for unsaturates in the C_2 mixture. A second method of treating the data assumes the mechanism, obtains k_3/k_2 from (III), $k_4/k_2^{1/2}$ from (I), and thus eliminates the necessity for a series of runs at each temperature.

The second method was used at Rochester and will be discussed first because of the apparent simplicity of interpretation of the results. The data for the investigation of the effect of temperature are in two groups, one at high intensity and one at lower intensity.

Both intensity ranges yield identical plots of log $k_4/k_2^{1/2}$ against $1/T$ (Fig. 1K); the least squares line yields $k_4/k_2^{1/2} = 1.9 \times 10^{-8} \exp(-7{,}300/RT)$ (molecules/cc.)$^{-1/2}$ sec.$^{-1/2}$. The scatter at low temperatures is doubtless due to the difficulty in accurately evaluating ΔR_{C_2}, which is small in this region and obtained from experimental measurements by two successive subtractions.

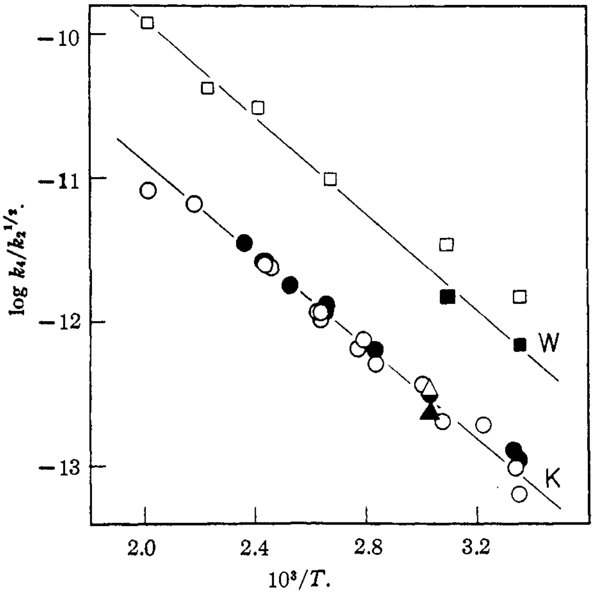

Fig. 1.—log $k_4/k_2^{1/2}$ against $1/T$, the line W has been displaced upward by one unit on the ordinate scale: □, slopes, Figs. 3 and 4; ■, slopes, Figs. 5 and 6; ○, $k_4/k_2^{1/2}$ calculated from equation I, AH-6; ●, $k_4/k_2^{1/2}$ calculated from equation I, S100; ▲, slope, $\Delta R_{C_2}/R_{C_4}$ Fig. 7; △, slope, R_{C_2}/R_{C_4} Fig. 7.

The Arrhenius plots (Fig. 2K) for k_3/k_2 by (III) are not linear but are of the same general shape with an upward curvature beginning at a lower temperature when lower I_{abs} is used. This suggests a second reaction producing C_2H_4 which becomes more important at higher temperatures for a given I_{abs}, and at lower I_{abs} for a given temperature. A reaction satisfying these conditions is

$$C_2H_4COC_2H_5 = C_2H_4 + CO + C_2H_5 \quad (7)$$

This reaction invalidates the assumptions necessary to derive equations (I) to (III), but a consideration of the magnitudes involved reveals that this is unimportant in the determination of $E_4 - {}^1/_2 E_2$; at low temperature the reaction has a low probability of occurrence, especially in view of the high intensities employed. At high temperature the difference ΔR_{C_2} is so large that the small increment in C_2H_4 necessary to account for the curvature in log ($R_{C_2H_4}/R_{C_4}$) *vs.* $1/T$ is negligible. Thus the difference $E_4 - {}^1/_2 E_2 = 7.3$ kcal./mole seems well founded.

A consideration of the material balance (C_4H_{10} + C_2H_6)/CO shows that, except for the two highest temperatures, the high intensity series was carried out under conditions such that reactions (1) to (5) completely account for all the products. This balance is obeyed only in a limited temperature range in the low intensity series. When this balance is obeyed, the ratio $R_{C_2H_4}/R_{C_4}$ may be taken as a true measure of k_3/k_2. Thus, from Fig. 2K, $E_3 - E_2 = 0$ kcal./mole, and the ratio

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[10] For detailed tables of data order Document 3356 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 $1.80 for photocopies (6 × 8 inches) readable without optical aid.

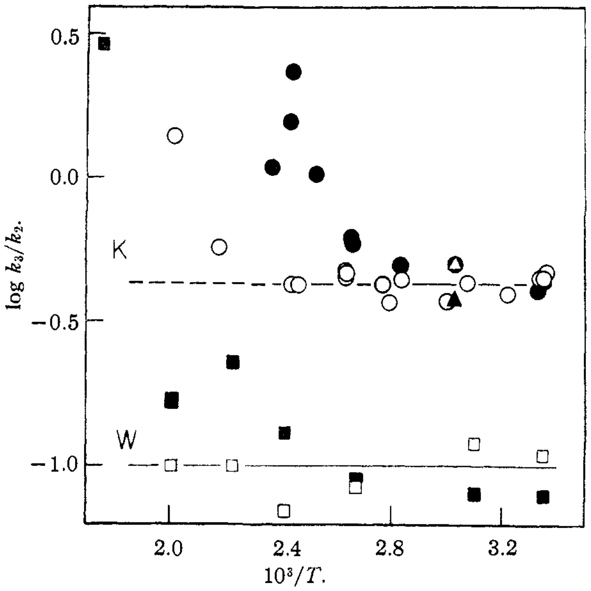

Fig. 2.—Log k_3/k_2 against $1/T$, the line K has been displaced upward by 0.5 unit on the ordinate scale: □, k_3/k_2 by intercepts, Figs. 3 to 6; ■, k_3/k_2 from average value of $R_{C_2H_4}/R_{C_4}$ at each temperature; O, k_3/k_2 from equation III, AH-6; ●, k_3/k_2 from equation III, S100; △, k_3/k_2 from average value of $R_{C_2H_4}/R_{C_4}$ at 56.8°; ▲, k_3/k_2 from intercept at 56.8°.

of the pre-exponential terms in the rate constant ratio is $A_3/A_2 = 0.14$.

Table II

°C.	Intercepts Figures 5 and 6	Intercepts Figures 3 and 4	k_3/k_2 intercepts	$R_{C_2H_4}/R_{C_4H_{10}}$
25	0.28	0.065	0.11	0.08 (0.09)
49.5	.30	.06	.12	.08
101	.24	.07	.085	.09 (0.10)
148.5	.14	(0)	(.07)	.13
176	.40	(.2)	(.10?)	.23
225	.50	(.3)	(.10?)	.18
297	?	?	?	2.9

Table III

Values of $k_4/k_2^{1/2}$

°C.	R_{C_2}/R_{C_4}	R_{C_4}/R_{C_4}
25	1.5×10^{-13}	0.7×10^{-13}
49.5	3.5×10^{-13}	1.5×10^{-13}
56	2.34×10^{-13}	3.25×10^{-13}
101	9.7×10^{-13}	11×10^{-13}
148.5	30.9×10^{-13}	32.6×10^{-13}
176	46×10^{-13}	51.4×10^{-13}
225	123×10^{-13}	132×10^{-13}

Figures 3 and 4 exhibit $\Delta R_{C_2}/R_{C_4}$ plotted against $(D)/R_{C_4}^{1/2}$, and Figs. 5 and 6 R_{C_2}/R_{C_4} against the same variable; the data for these plots were obtained from Natl. Res. Council. The origin in Figs. 3 to 6 has been displaced upward by one ordinate scale unit for each higher temperature; thus in Fig. 3 the origin for the lines at 25, 49.5 and 101° occur, respectively, at 0.0, 0.1 and 0.2 on the ordinate scale. Abscissa variation has been obtained primarily by changing pressure at constant I_0, although the low intensity runs of Table I have been included. Similar plots at 56° are obtained from the experiments carried out at Rochester and are shown in Fig. 7. This plot was obtained by variation of I_{abs} at constant ketone concentration. At all temperatures straight lines are obtained, confirming the general validity of the reaction scheme.

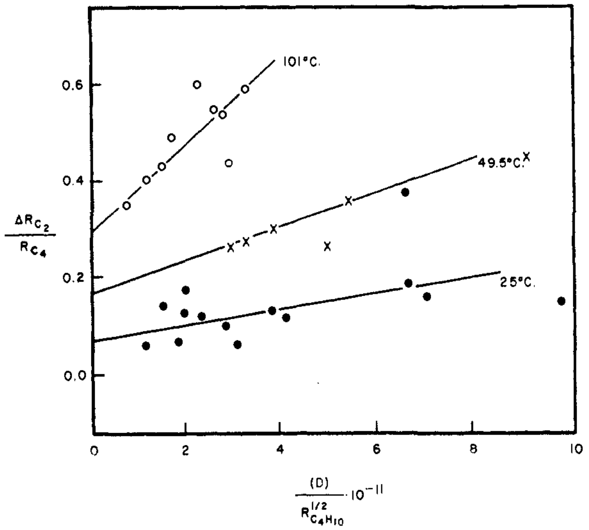

Fig. 3.—$\Delta R_{C_2}/R_{C_4}$ [against $(D)/R_{C_4}^{1/2}$] at 25, 49.5 and 101°. The origins for the lines at 25, 49.5 and 101° occur, respectively, at 0.0, 0.1 and 0.2 on the ordinate scale.

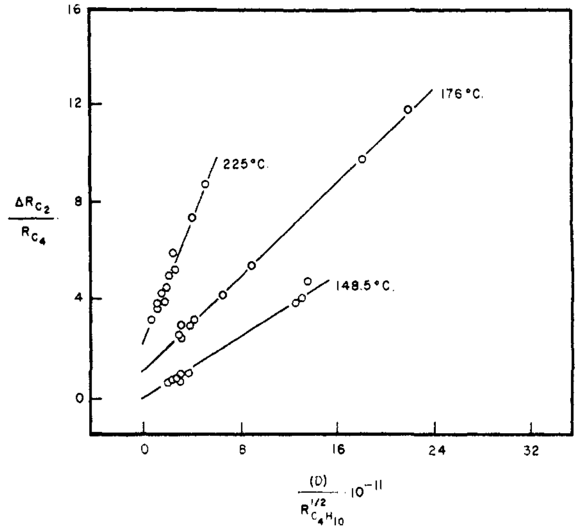

Fig. 4.—$\Delta R_{C_2}/R_{C_4}$ against $(D)/R_{C_4}^{1/2}$ at 148.5, 176 and 225°. The origins for the lines at 148.5, 176 and 225° occur, respectively, at 0, 1 and 2 on the ordinate scale.

The plot of $\Delta R_{C_2}/R_{C_4}$ should, by equation (1), pass through the origin; this property is exhibited in Fig. 7. Fig. 3, however, shows small positive intercepts of order 0.1 (dimensionless), which may also exist at the higher temperatures (Fig. 4) although the data in this temperature region are not sufficiently accurate to allow the evaluation of quantities of this magnitude. The absence of such intercepts when I_{abs} is varied at constant (D), Fig. 7, and their apparent presence when pressure is varied at constant I_0, might be interpreted as a third body requirement for butane formation. Such a concept has been reiterated recently in a discussion of a

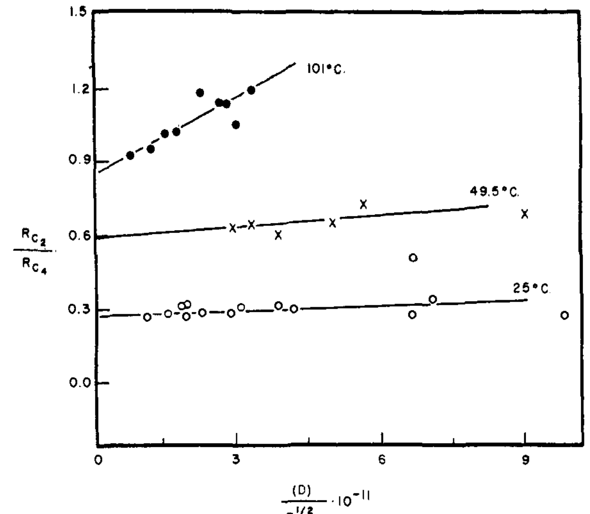

Fig. 5.—R_{C_2}/R_{C_4} against $(D)/R_{C_4}{}^{1/2}$ at 25, 49.5 and 101°. The origins for the lines at 25, 49.5 and 101° occur, respectively, at 0.0, 0.1 and 0.2 on the ordinate scale.

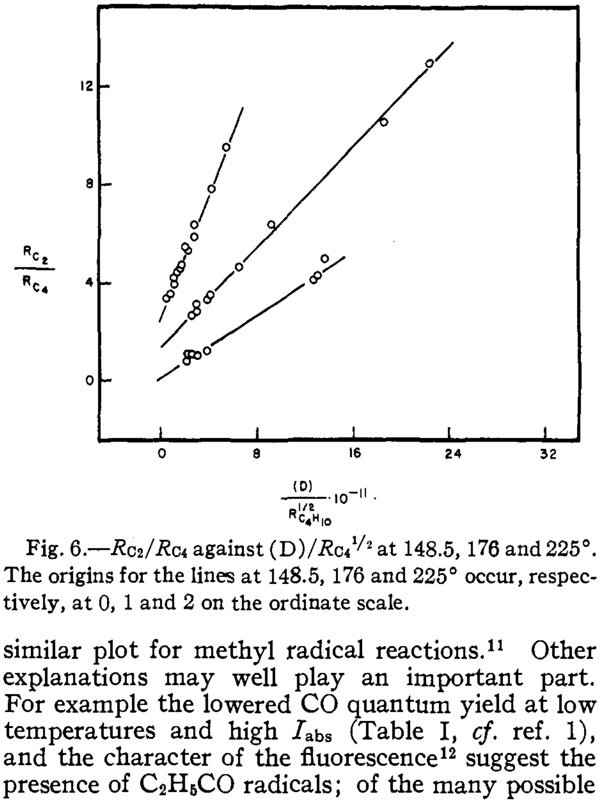

Fig. 6.—R_{C_2}/R_{C_4} against $(D)/R_{C_4}{}^{1/2}$ at 148.5, 176 and 225°. The origins for the lines at 148.5, 176 and 225° occur, respectively, at 0, 1 and 2 on the ordinate scale.

similar plot for methyl radical reactions.[11] Other explanations may well play an important part. For example the lowered CO quantum yield at low temperatures and high I_{abs} (Table I, *cf.* ref. 1), and the character of the fluorescence[12] suggest the presence of C_2H_5CO radicals; of the many possible reactions of these radicals, a reaction with an ethyl could lead to a higher value of $\Delta R_{C_2}/R_{C_4}$ than predicted by the mechanism at low values of $(D)/R_{C_4}{}^{1/2}$, as required by Fig. 3. A more detailed discussion is not warranted by the accuracy of the data available at present.

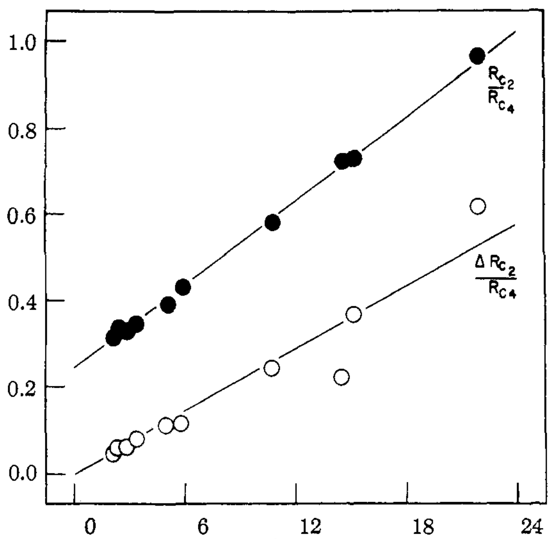

Fig. 7.—$\Delta R_{C_2}/R_{C_4}$ and R_{C_2}/R_{C_4} against $(D)/R_{C_4}{}^{1/2}$ at 56.8°.

The intercepts observed in Figs. 5 and 6 should yield $2k_3/k_2$; the extraneous intercepts in Figs. 3 and 4 must first be subtracted, however. Thus if the intercept of $\Delta R_{C_2}/R_{C_4}$ is a, the intercept of R_{C_2}/R_{C_4} will be given by $2k_3/k_2 + a$. The results of these calculations are given in Table II with the uncertain high temperature intercepts and calculations based on them being bracketed in columns 3 and 4. These computations yield $k_3/k_2 = 0.1$, independent of temperature, Fig. 2W.

Column 5 of Table II shows the arithmetical average of the values of $R_{C_2H_4}/R_{C_4}$ at each temperature from the data obtained at Natl. Res. Council; the values in brackets were obtained by K. J. Ivin in another apparatus. A plot of log $(R_{C_2H_4}/R_{C_4})$ *vs.* $1/T$ from these data is also shown in Fig. 2W; the same general trend as in Fig. 2K is observed, again indicating the necessity of postulating reaction (7). The lower value of $\log(R_{C_2H_4}/R_{C_4})$ at 225°, $10^3/T = 2$, is doubtless due to the higher I_{abs} used at this temperature. The ratio $R_{C_2H_4}/R_{C_4}$ increases with pressure; this effect is particularly noticeable at 225° where absorbed intensity is approximately constant. Thus combining the pressure effect and the intensity effect mentioned previously, the ratio $R_{C_2H_4}/R_{C_4}$ increases with $(D)/R_{C_4}{}^{1/2}$ as required by the mechanism to a first approximation.

The slopes of the lines in Figs. 3 to 6 yield values of $k_4/k_2{}^{1/2}$ at the various temperatures; these are collected in Table III. The slightly higher results obtained from Figs. 5 and 6 are explicable in terms of the occurrence of reaction (7). At the higher temperatures this difference is negligible in a calculation of $E_4 - {}^1/_2\,E_2$; at the lower temperatures it is clear from an examination of Fig. 3 that the slopes of Fig. 5 are more reliable. This is indicated in Fig. 1W, (log $(k_4/k_2{}^{1/2})$ *vs.* $1/T$), by drawing the line through the points from Fig. 5, although the values from Fig. 3 are also plotted. In the 10 runs at 297° so little butane was formed that large errors in its measurement were unavoidable in the apparatus used. Equations (I) and (II) have not been plotted at this temperature and a calculation of $k_4/k_2{}^{1/2}$ by (I) yields values varying between 140 and 316 $\times 10^{-13}$ (molecules/cc.)$^{-1/2}$sec.$^{-1/2}$; this temperature does not appear in Fig. 1W. An activation energy difference $E_4 - {}^1/_2\,E_2 = 7.5$ kcal./mole is obtained.

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It is apparent that the activation energy differences obtained from the two sets of data are in excellent agreement. However, the disagreement with the results of Dorfman and Sheldon[2] ($E_3 - E_2 = 4.8$ kcal./mole; $E_4 - {}^1/_2 E_2 = 4.1$ kcal./mole) is marked. Certainly the value of $E_3 - E_2$ given by Dorfman and Sheldon is subject to considerable error because of the large extrapolation in their plots of equation (2) from the low intensity region in which their work was carried out to a zero value of the abscissa. Their method of variation of I_{abs} at essentially constant (D) is shown to be free of extraneous intercepts by Fig. 7 of this work. They did, however, work in an intensity interval in which reaction (7) is certain to be of importance at 120° and may also contribute appreciably at 56°. In a fairly small intensity interval this will have the effect of an over-all upward displacement of the plot of equation (II), leading to high values of the intercept. Further, their assumption of linearity in the plot of log ($R_{C_2H_4}/R_{C_4}$) *vs.* $1/T$, *i.e.*, the neglect of reaction (7), is now known to be incorrect, and their choice of temperatures was such as to take one point off each arm of the curve; this procedure naturally leads to values of $E_3 - E_2$ which are too high. Overemphasis of the temperature coefficient of the C_2 rate by disproportionation will automatically lead to a low value for $E_4 - {}^1/_2 E_2$.

The value of $E_3 - E_2$ obtained in this work is in much better agreement with the 0.8 kcal./mole obtained by Ivin and Steacie[13] from a study of the photolysis of mercury diethyl, and with the $E_3 \leqslant 1.2$ kcal./mole obtained by LeRoy and Kahn.[14]

By use of reasonable values for the collision diameters of diethyl ketone and an ethyl radical, 6 and 4×10^{-8} cm., respectively, the steric factor ratio $p_4/p_2^{1/2}$ may be calculated from the rate constant ratios given here; the result is $p_4/p_2^{1/2} \approx 10^{-3}$. A more exact calculation requires a knowledge of the true reaction volume. Some experiments done at Rochester indicate that a diffusion effect must be taken into account under conditions used in this work; further calculations would thus seem unwarranted at the present. It is, however, interesting to note that this result is quite similar to the analogous ratio for methyl radical reactions.[15,16]

Any discussion of the disproportionation reaction of ethyl radicals is incomplete without some comment on the variation of the ratio ethylene–butane observed in various systems.[17] Even the relatively well understood sources of this radical lead to remarkably divergent values. This work finds $k_3/k_2 \approx 0.1$, independent of temperature in the range 25 to 225°; the photolysis of propionaldehyde[18] yields a value 0.1 at 25°. The ratio of $R_{C_2H_4}/R_{C_4H_{10}}$ from methyl ethyl ketone[18,19] has a value slightly less than 0.2 at low temperature and increases with temperature in a manner similar to that in Figs. 2k and 2w; a value of $k_3/k_2 = 0.1$ to 0.2 and a reaction analogous to (7) form a feasible explanation. The value $A_3/A_2 = 0.4$ obtained by Ivin and Steacie[13] is probably different beyond experimental error. Further, a similar paradox exists for *n*-C_3H_7 radicals; Blacet and Calvert[20] find 10% disproportionation of *n*-propyl radicals from *n*-butraldehyde at 25°; di-*n*-propyl ketone[21] yields 15–20% at 113°. Thermal and wall effect greatly reduce the significance of the results found in the mercury compound.[22] By analogy, it would seem reasonable to attach more significance to the value $A_3/A_2 \approx 0.1$ for ethyl radicals.

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OTTAWA, CANADA AND ROCHESTER, N. Y.

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