Rate of Association of nPropyl Radicals

S. G. Whiteway and C. R. Masson

Although the detailed explanation of the breadth of some of the low-temperature spectra is still not clear, sufficient data have been collected to allow some empirical observations. At 20°K, the spectrum of the mixed crystalline solid solution is sharp if the spectrum of the host crystal itself is sharp. The sharpness depends more on the environment (host) than on the molecule (guest). Thus, naphthalene has a sharp crystal absorption and fluorescence spectrum at 20°K (~ 10 cm^{-1} line width). The absorption and fluorescence spectra of azulene, anthracene, and tetracene, and the phosphorescence spectra of the β-halonaphthalenes are all sharp in mixed crystals with naphthalene at 20°K. The absorption and fluorescence spectra of phenanthrene and of anthracene crystals are much broader than the spectra of naphthalene crystals at 20°K. The spectra of anthracene in phenanthrene or tetracene in anthracene are also less sharp than the spectra of anthracene or of tetracene in naphthalene. As further

evidence, the absorption and fluorescence spectra of durene crystal are fairly sharp at 20°K; the absorption and fluorescence of naphthalene in durene and the phosphorescence spectra of impurities in durene are also sharp at 20°K.

Thus, in the case of the β-halonaphthalenes studied in this work, it is perhaps not surprising to find that the phosphorescence spectrum of a mixed crystal of β—I—N in β—Cl—N is broad at 20°K, since the phosphorescence spectrum of the β—Cl—N crystal is broad at 20°K.

A more complete theory of the electronic structure of molecular crystals and the mechanism of energy migration in crystals and mixed crystals should be able to account for the observed line widths in the low-temperature spectra of these substances.

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Rate of Association of n-Propyl Radicals*

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The rate of association of n-propyl radicals has been measured by studying the photolysis of di-n-propyl ketone in intermittent light. A value of $k_2'=1\times10^{-8}$ cc molecule^{-1} sec^{-1} at 100° has been obtained. Possible sources of error have been discussed and it is concluded that the above value may be too high by a factor of the order of 20, thus indicating that reaction probably occurs at every collision. A value of $k_3/k_2=0.125$ ±0.01 has been found, where k_3 and k_2 are the rate constants for disproportionation and combination, respectively.

CONSIDERABLE progress has been made in recent years in determining the rates of elementary reactions involving free radicals.[1] The relative rates of many such reactions have now been measured, and several studies have been devoted to the determination of absolute rate constants. In particular, the rates of combination of methyl[2-6] and ethyl[7] radicals have recently been investigated. Association reactions of this type are useful as "reference" reactions with which the rates of other reactions of the same radical species can

be compared. It was the purpose of the present work to extend these studies to the combination and disproportionation of n-propyl radicals.

The method employed was to study the photolysis of di-n-propyl ketone in intermittent light, using the rotating sector technique of Dickinson.[8] The photolysis of this ketone has been studied previously by Bamford and Norrish[9] and the kinetics have recently been reinvestigated.[10] It has been shown that two types of primary processes occur:

$$C_3H_7COC_3H_7+h\nu \begin{cases} \rightarrow 2C_3H_7+CO & (1a) \\ \rightarrow C_2H_4+CH_3COC_3H_7. & (1b) \end{cases}$$
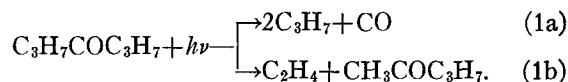
The n-propyl radicals formed in reaction (1a) can combine or disproportionate according to reactions (2)

* National Research Council.

[1] See E. W. R. Steacie, *Atomic and Free Radical Reactions* (Reinhold Publishing Corporation, New York, 1954), second edition.

[2] G. B. Kistiakowsky and E. Kirk Roberts, J. Chem. Phys. 21, 1637 (1953).

[3] K. U. Ingold and F. P. Lossing, J. Chem. Phys. 21, 308 (1953).

[4] R. W. Durham and E. W. R. Steacie, J. Chem. Phys. 20, 582 (1952).

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[6] D. M. Miller and E. W. R. Steacie, J. Chem. Phys. 19, 73 (1951).

[7] K. J. Ivin and E. W. R. Steacie, Proc. Roy. Soc. (London) A208, 25 (1951).

[8] R. G. Dickinson in W. A. Noyes, Jr., and P. A. Leighton, *The Photochemistry of Gases* (Reinhold Publishing Corporation, New York, 1941), pp. 202–209.

[9] C. M. Bamford and R. G. W. Norrish, J. Chem. Soc. 1504 (1935); 1531, 1544 (1938).

[10] C. R. Masson, J. Am. Chem. Soc. 74, 4731 (1952).

TABLE I. Nonsector runs. (d.p.k.) $= 4.15 \times 10^{17}$ molecules cc^{-1}.

Run	Duration of run (sec)	Rates (molecules cc^{-1} sec^{-1}) $\times 10^{-12}$ CO	ΔC_3H_8	C_3H_6	C_6H_{14}	$\dfrac{R_{CO}}{R_{C_2H_4}}$
(A) Temp. = 117°C						
1[a]	600	55.4	...	...	42.2	1.000
2[b]	1200	44.4	...	...	35.7	1.000
3[b]	1200	50.6	...	...	40.5	1.000
(B) Temp. = 100°C						
8[c]	1200	39.8	...	...	36.1	1.047
10[c]	900	50.4	...	...	45.1	1.097
11	1200	56.1	...	...	49.8	1.004
12	1200	75.2	...	...	61.4	1.010
13	900	71.3	...	...	69.0	1.026
25	900	95.8	8.23	8.82	...	0.992
27	900	85.7	7.92	8.28	...	0.992
30	900	79.3	6.33	7.89	...	0.997
32	900	78.8	5.42	8.34	...	1.013
35[d]	2700	81.0	6.29	7.77	...	1.020
36[d]	2700	78.4	5.94	7.64	...	1.014
37[d]	2700	85.4	6.56	8.91	...	0.997
38[d]	2700	68.7	4.57	7.85	...	0.985
40[d]	2700	95.3	8.49	9.03	...	1.000
44[e]	1200	54.7	4.21	6.18	45.4	1.013
45[f]	2700	20.8	1.93	2.32	16.43	1.045
46[g]	1200	64.2	4.20	7.23	54.6	1.029
49	900	69.7	4.93	7.80	...	1.019
50	900	74.0	5.22	8.50	...	1.018
51	900	72.5	4.75	8.42	...	0.997
55	900	64.0	4.31	7.21	...	1.005
57	900	69.0	4.37	8.00	...	1.021
60	900	62.7	4.79	6.52	...	1.023
62	900	82.6	5.40	8.45	...	1.029
64	900	71.0	5.87	7.70	...	1.000
66	900	72.9	4.85	7.59	...	1.028
68	900	65.3	4.44	7.09	...	1.022
73[e]	1200	42.6	2.02	5.28	...	1.026
75[e]	1800	37.7	2.34	3.65	...	1.029
76[e]	1200	56.6	4.12	5.85	...	1.026
77[h]	1500	29.6	1.85	3.61	...	1.000
78[h]	1500	28.8	1.80	3.49	...	0.984
79[h]	1500	27.9	1.78	3.24	...	1.000
80[e]	1200	47.0	2.92	5.49	...	1.007
(C) Temp. = 150°C						
81	910	70.2	9.99	6.62	56.0	0.975
82	900	65.7	9.02	6.16	55.5	0.981
83[h]	1800	25.1	4.31	2.45	19.8	1.030

[a] (d.p.k.) = 3.67 × 10¹⁷.
[b] (d.p.k.) = 3.76 × 10¹⁷.
[c] (d.p.k.) = 4.23 × 10¹⁷.
[d] Very slow sector runs. Data shown multiplied by three.
[e] 60% transmission neutral density filter.
[f] 25% transmission neutral density filter.
[g] 1 cm 4 N acetic acid filter.
[h] 40% transmission neutral density filter.

and (3), respectively,

$$2C_3H_7 \rightarrow C_6H_{14}, \qquad (2)$$

$$2C_3H_7 \rightarrow C_3H_6 + C_3H_8, \qquad (3)$$
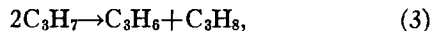
and experimental conditions can be arranged so that these reactions predominate over other possible reactions of radicals in the system.

The method of determining the velocity constants k_2 and k_3 was similar in principle to that described by Gomer and Kistiakowsky.[5] If (1), (2), and (3) are the only reactions which occur, then x, the steady-state concentration of propyl radicals is given by

$$x = (R_{CO}/k_2 + k_3)^{\frac{1}{2}}, \qquad (4)$$

and sector experiments may be performed to find θ, the mean lifetime of the radicals, as defined by

$$\theta = \frac{\text{number of radicals/cc}}{\text{number of radicals appearing/cc/sec}}$$

in the steady state.

The numerator of this expression is x, while the denominator is given by

$$+dx/dt = 2R_{(CO)}.$$

Thus,

$$k_2 + k_3 = k_2' = \frac{1}{4\theta^2 R_{(CO)}}, \qquad (5)$$

where k_2', the sum of the rates of combination and disproportionation, may be taken as equal to the rate of association of two propyl radicals to give some intermediate complex which may then either be stabilized to yield hexane or disproportionate to give propylene and propane.

The lifetime θ is found by comparing an experimental plot of x_i/x_s versus Δt (the time for one light flash in units of seconds) with a theoretical plot of x_i/x_s versus $\Delta \tau$ (the time for one flash in units of lifetimes). Here x_i and x_s are respectively the steady-state propyl radical concentrations in intermittent and steady light. In order to determine the experimental x_i/x_s ratios it is necessary to have a "pilot"[11] reaction giving a measurable product whose rate is directly proportional to x. In the present work experimental conditions were adjusted to that the abstraction reaction

$$C_3H_7 + C_3H_7COC_3H_7 \rightarrow C_3H_8 + C_3H_6COC_3H_7 \quad (6)$$
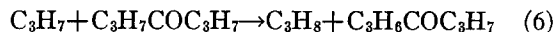
takes place to a small but measurable extent. This gives

$$\Delta R_{(C_3H_8)} = k_6(x)(C_3H_7COC_3H_7).$$

The rate of propane production by step (6), $\Delta R_{(C_3H_8)}$ is proportional to x, so that

$$x_i/x_s = \Delta R(C_3H_8)_i/\Delta R(C_3H_8)_s.$$

The abstraction step, and further reactions of the $C_3H_6COC_3H_7$ radical will alter the simple relationship of x to $R_{(CO)}$ [Eq. (4)] to a certain extent. This will be discussed later.

Experimental

The ketone (Eastman Kodak Company White Label) was stored over Drierite for three months, then distilled in an atmosphere of nitrogen through a 12 plate column, the middle fraction being retained. Samples were degassed at about $-50°$ before use.

The quartz reaction cell was 20 cm long and 2 cm

[11] O. K. Rice, J. Chem. Phys. 10, 440 (1942).

i.d., with a measured volume of 60 cc. It was surrounded by an aluminum block furnace, the temperature of which was controlled to ±0.5° with a photoelectric relay operating on the light beam from a galvanometer, the latter being actuated by a thermocouple near the reaction cell. A cathetometer was used to read pressures registered by a mercury manometer of 4-mm diam precision bore tubing, attached to the reaction system. The latter, of total volume 92 cc was isolated from the remainder of the apparatus by a float valve mercury cutoff. Since the vapor pressure of the ketone at 30° is only about 10 mm, all parts of the reaction system external to the furnace were electrically heated to about 80°.

The light source was a General Electric AH-6 mercury arc operated on direct current as described elsewhere.[12] The unfiltered light which emerged from a slit, 2 mm wide, in the lamp housing, was collimated by a system of stops and quartz lens into a nearly parallel beam which just filled the reaction cell. The intensity was varied in some experiments by means of neutral density filters of coated quartz.

The 14-in. diameter sectors were made from $\frac{1}{16}$-in. aluminium sheet, cut so as to allow the passage of light for $\frac{1}{3}$ of the time ($p=2$). Two- and four-slotted sectors were used, the latter for the shorter flash times. The sectors were made to chop the light beam near the source, with the edge of the slot parallel to the slit in the lamp housing. Thus the "penumbra" effect[13] was probably not important. The sectors were driven by a constant speed motor through a train of fixed and variable Metron Speed Changers. Flash times were measured stroboscopically or calculated from gear settings.

The gaseous products of the reaction were pumped off and measured by means of a combined Töpler pump, McLeod gauge, and gas buret. The CO was removed through a pumped-down liquid nitrogen trap at −210°. The C_2H_4 was pumped off from a train of two Ward-LeRoy stills at −175°, the C_3 fraction at −135° and n-hexane at −95°. The C_3 fraction was further analyzed for C_3H_6 and C_3H_8 by using the hydroxy-mercurial method[14] in a Blacet-Leighton[15] apparatus. The quantity ΔC_3H_8 was calculated by subtracting twice the C_3H_6 from the total C_3.

For most runs the temperature was 100° and the ketone concentration was 4.15×10^{17} molecules/cc. These conditions, together with the high light intensity, gave a $C_6H_{14}/\Delta C_3H_8$ ratio of about 10, which is probably high enough so that termination steps, first order with respect to C_3H_7 radicals, could be considered unimportant as a first approximation.

[12] S. G. Whiteway and C. R. Masson, Can. J. Chem. **32**, 1154 (1954).
[13] W. G. Burns and F. S. Dainton, Trans. Faraday Soc. **46**, 411 (1950).
[14] Pyke, Kahn, and LeRoy, Anal. Chem. **19**, 65 (1947).
[15] F. E. Blacet and P. A. Leighton, Ind. Eng. Chem. Anal. Ed. **3**, 266 (1931).

TABLE II. Sector runs. (d.p.k.)$=4.15\times10^{17}$ molecules cc^{-1}. Temp.$=100°$C. Duration of each run$=2700$ sec.

Run	Flash time (sec) $\times10^3$	Rates (molecules cc^{-1} sec^{-1}) $\times10^{-12}$			$\dfrac{R_{CO}}{R_{C_2H_4}}$	$\dfrac{\Delta R_{(C_3H_8)i}}{\Delta R_{(C_3H_8)s}}$	ψ
		CO	ΔC_3H_8	C_3H_6			
26	9.57	29.9	2.87	2.98	1.010	0.378	5.259
28	9.45	27.5	2.66	2.88	1.000	0.416	5.236
29	5.07	28.1	2.67	2.84	1.024	0.404	4.970
31[a]	4.30	28.3	2.79	2.88	1.019	0.413	4.900
33	21.28	28.8	2.45	3.00	1.019	0.353	5.599
35	833.3	27.0	2.10	2.59	1.020	0.338	7.177
36	833.3	26.1	1.98	2.55	1.014	0.338	7.170
37	833.3	28.5	2.19	2.97	0.997	0.322	7.188
38	833.3	22.9	1.52	2.62	0.985	0.318	7.141
40	833.3	31.8	2.83	3.01	1.000	0.333	7.212
41	6.10	30.5	3.10	3.30	1.015	0.399	5.068
43	5.13	28.8	2.61	3.43	1.000	0.376	4.980
53[b]	3.68	25.0	2.43	2.47	1.033	0.446	4.805
54[b]	3.70	23.0	2.12	2.82	1.019	0.439	4.790
56[b]	5.46	23.5	2.06	2.82	1.022	0.412	4.963
58[b]	13.32	21.0	1.54	2.57	1.018	0.360	5.326
59[b]	8.00	21.5	1.85	2.59	1.019	0.420	5.110
63	66.6	26.2	2.15	2.74	1.020	0.368	6.073
65	27.0	25.2	1.99	2.99	1.002	0.359	5.673
69	166.6	21.6	1.48	2.36	1.010	0.333	6.430
72[b,c]	3.00	13.5	1.20	1.62	1.050	0.472	4.583
74[b,c]	2.94	16.0	1.44	1.61	1.180	0.470	4.611

[a] Duration of run $=2238$ sec.
[b] Sector with four slots. Other runs, sector with two slots.
[c] Duration of run $=3600$ sec.

RESULTS

The complete results are presented in Tables I and II, which represent the data for experiments under steady and intermittent light, respectively. Included in Table I are the results of five experiments at very slow sector speeds (flash time 0.8333 sec); for comparison with other data the rates for these runs have been multiplied by a factor of three. The numbers of the runs in Tables I and II indicate the order in which experiments were performed.

There are two ways in which the theoretical upper limit of x_i/x_s (0.578 with the sectors employed here) may be approached experimentally: (a) decreasing the flash time by either increasing the rpm of the sector or increasing the number of slots, and (b) decreasing the light intensity. The latter was accomplished in some runs by the use of neutral density filters. In addition, run-to-run variations in light intensity are inherent in the AH-6 arc.

These two sources of variation in I_{abs} necessitated a correction procedure before a value of θ and a corresponding value of $R_{(CO)}$ could be determined for substitution in Eq. (5). This correction was done in two parts: (a) an experimental value of x_i was associated with an interpolated value of x_s at the same light intensity to give a value of x_i/x_s, and (b) these values of x_i/x_s were then plotted against a function of flash time according to the particular value of $R_{(CO)}$ associated with each one.

For the first correction a normalization plot was made of $\Delta R(C_3H_8)_s$ *versus* $R_{(CO)}$ from the data of Table I. It was then a simple matter to interpolate graphically to find what $\Delta R(C_3H_8)_s$ would be at the
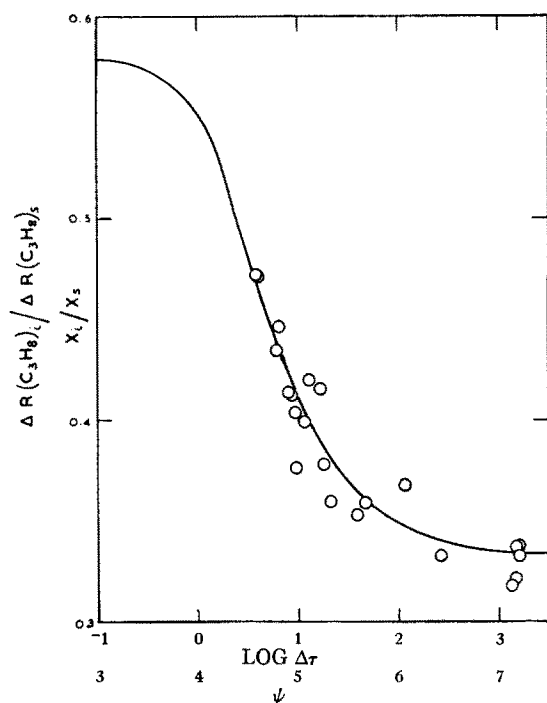
FIG. 1. Plot of $\Delta R_{(C_3H_8)i}/\Delta R_{(C_3H_8)s}$ against ψ. Solid line, theoretical curve of x_i/x_s against $\log\Delta\tau$.

light intensity corresponding to a particular sector run, i.e., at $R(CO)_s = 3R(CO)_i$. The values of x_i/x_s obtained in this way are included in Table II.

For the second correction, it follows from Eq. (5) that

$$\log(2\theta) + 0.5 \log R(CO)_s = 0.5 \log(1/k_2').$$

The theoretical sector plot is $\log(\Delta\tau)$ *versus* x_i/x_s, where $\Delta\tau$ is the number of lifetimes per flash. If the experimental plot is taken as $\log(2\Delta t) + 0.5 \log R(CO)_s = \psi$ (where Δt is the flash time in seconds), *versus* $\Delta R(C_3H_8)_i/\Delta R(C_3H_8)_s$, then the particular value of ψ (let us call it ψ_0) corresponding to $\log(\Delta\tau) = 0$ is the value of ψ when $\Delta\tau = 1$, that is, when one flash time equals one lifetime. This means that here $\theta = \Delta t$, and we can write

$$\psi_0 = \log(2\Delta t) + 0.5 \log R(CO)_s = 0.5 \log(1/k_2').$$

In this manner a value of k_2' is calculated which is automatically corrected for variations in light intensity.

The values of ψ, defined above, are listed in Table II. Figure 1 shows the experimental plot of $\Delta R(C_3H_8)_i/\Delta R(C_3H_8)_s$ *versus* ψ. The solid line is the theoretical curve of x_i/x_s *versus* $\log(\Delta\tau)$. The highest points on the sector curve $((x_i/x_s) = 0.47)$ were obtained with a four-slotted sector at 1700 rpm and a 60% transmission neutral density filter. In order to do experiments at $\psi = 4.0$ with this sector, either the light intensity would have to be decreased some thousand-fold, or the rpm would have to be raised to about 7000. Neither of these alternatives, or a compromise, was feasible, nor was it

considered wise to increase the number of slots. Hence no attempt was made to obtain points nearer the "plateau" of the sector curve.

From Fig. 1 it is evident that

$$\psi_0 = 4.0 = 0.5 \log(1/k_2')$$

so that $k_2' = 1 \times 10^{-8}$ cc molecule^{-1} sec^{-1} at $100°$.

DISCUSSION

The collision theory value of k_2', assuming zero activation energy for reactions (2) and (3) and a value of 6.5 A for the collision diameter, σ, of a propyl radical, is 4×10^{-10} cc molecule^{-1} sec^{-1} at $100°$. The experimental value is thus about 25 times higher than expected on the basis that reaction occurs at every classical collision. It is also higher, by the same order of magnitude, than the value calculated from the theory of absolute reaction rates.[16] Estimating $\alpha = 64 \times 10^{-25}$ cc for the polarizability factor and taking Stevenson's value[17] of $\rho = 7.9$ ev for the ionization potential of n-propyl radical, this theory yields a value of k_2' of 3.2×10^{-10} cc molecule^{-1} sec^{-1} at $100°$ (neglecting the electronic multiplicity factor).

In examining possible sources of error for this result, it is reasonable to conclude that any uncertainties in the values chosen for σ or α and ρ above would contribute little to the discrepancy between the calculated and observed values of k_2'. The value of σ for example, would have to be five times larger than that chosen to obtain agreement between the two quantities.

The discrepancy is also larger than the error introduced by the simplifying assumption that reaction (4), and other termination processes which are first order with respect to propyl radicals, do not influence the simplified kinetic scheme as depicted by (1), (2), and (3) above. Comparison with the work of Kistiakowsky and Roberts,[2] however, would indicate that the experimental value of k_2' may have to be lowered by perhaps 50% to correct for the effect of such processes. Secondary reactions of this nature lead to a dependence of x on $R(CO)$ of the type $x \propto R^n_{(CO)}$, where $0.5 < n < 1.0$. For the simple sector theory to hold, n should approach the value 0.5. That this is nearly true in the present case is shown by the first power proportionality of C_3H_6 and C_6H_{14} to CO (Tables I and II).

The most probable source of error in the present work is associated with the difficulty of determining accurately $\Delta R(C_3H_8)$. This is obtained as the difference between two quantities each of which is several times larger than $\Delta R(C_3H_8)$ itself. In practice, the algebraic sum of three experimental errors is involved in the determination of this quantity. To reduce these errors to a minimum, the photolyses were carried to higher conversions (*ca* 20%) than would normally be employed.

[16] Glasstone, Laidler, and Eyring, *The Theory of Rate Processes* (McGraw-Hill Book Company, Inc., New York, 1941).
[17] D. P. Stevenson, Trans. Faraday Soc. 49, 867 (1953).

Under these conditions the possibility of further secondary reactions and their influence on the simple square root dependence of $[C_3H_7]$ on $R(CO)$ must be considered. That these do not occur to an appreciable extent is shown by the shape of the sector curve itself. If $[C_3H_7]$ were directly proportional to $R(CO)$, the values of x_i/x_s would show no variation with flash time; the actual data are reasonably consistent with the long and short flash time limits of 0.333 and 0.578, respectively, associated with the relationship $[C_3H_7] \propto R^{0.5}_{(CO)}$.

That secondary reactions do, however, appear to occur to some extent is indicated by a direct plot of $\Delta R(C_3H_8)$ *versus* $R(CO)$ from the results in Table I. The exponent is apparently of the order of unity, in contradiction to the observations above. Critical examination of the experimental data reveals no adequate explanation for this. The only possibility which can be suggested is that the C_3 fraction may contain small quantities of some other product (e.g., C_4H_{10}) which would pass undetected with our analytical procedure. Further work, using more sensitive analytical methods, would be required to check this, but rough calculations indicate that possible reactions arising from the secondary photolysis of methyl propyl ketone, formed in primary step 1(b), might occur to an extent sufficient to give the observed effect. It is estimated that the effect of such reactions might be to increase the observed value of k_2' by a factor as high as ten. It is of interest to note that a reaction such as

$$CH_3 + C_3H_7 = C_4H_{10},$$
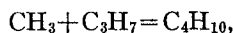
which is first order with respect to propyl radicals, could be included in the "pilot" reaction without seriously influencing the shape of the sector curve.

A further indication that the observed values of $\Delta R(C_3H_8)$ may be too high is afforded by measurements of the ratio $k_4/k_2^{\frac{1}{2}}$, calculated from the quantity $\Delta R(C_3H_8)/R^{\frac{1}{2}}(C_6H_{14})$ (d.p.k.). The mean value obtained from three runs at 100° is 1.34×10^{-12}, which is significantly higher than the value of 0.91×10^{-12} calculated from previous results.[10] At 150°, on the other hand, good agreement is obtained with previous data.

The above are very sensitive indications of secondary reactions. Other aspects of the photolysis indicate that such processes are virtually negligible. Thus the ratio CO/C_2H_4 obtained here is essentially constant for all runs, in line with earlier conclusions that these products arise in two independent primary processes. The mean value of this ratio (1.02 ± 0.02 at 100°) is lower than

TABLE III. Summary of values for k_3/k_2.

Temperature °C	k_3/k_2	Estimated error	Reference
20	0.13	±0.02	a
25	0.11	±0.02	a
100	0.136	±0.01	this work
113	0.21	±0.1	(10)
150	0.118	±0.01	this work
175	(0.06)	⋯	a

a F. E. Blacet and J. G. Calvert, J. Am. Chem. Soc. **73**, 661 (1951).

the value of 1.45 obtained previously. This is undoubtedly due to the higher proportion of short wavelength radiation in the light source employed here. Blacet and his co-workers[18] have shown that, for the aliphatic aldehydes, intramolecular primary processes become relatively more important at short wavelengths; the same may also be true of the higher ketones.

The values of k_3/k_2, derived from the ratio $R(C_3H_6)/R(C_6H_{14})$, are of the same order of magnitude as those found by other workers. Table III summarizes the values of this ratio at present in the literature. These are consistent with a zero difference in activation energy between reactions (2) and (3). From Table III, the most probable value of k_3/k_2 is estimated to be 0.125 ±0.01.

In view of the complexity of the reaction scheme, the possibility for secondary reactions in this photolysis at high light intensities, and the marked sensitivity of the sector plot to small errors in ΔC_3H_8, the high value obtained for k_2' is probably not too serious. The combined experimental errors above indicate that the value of k_2' probably lies close to the kinetic theory and absolute rate theory values with a steric factor and transmission coefficient, respectively, of unity.

The result is of interest when compared with the values obtained for the rates of association of methyl and ethyl radicals. For the former, a steric factor close to unity now seems to be definitely established.[2] For ethyl radicals a value of about 10^{-1} has been obtained, and recent work[19] has confirmed this order of magnitude. The absence of any downward trend with increasing complexity of the radicals suggests that a high collision yield may be characteristic of many radical association reactions.

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[18] See F. E. Blacet and J. N. Pitts, Jr., J. Am. Chem. Soc. **74**, 3382 (1952).
[19] A. Shepp and K. O. Kutschke, J. Chem. Phys. (to be published).