323. *The Reactions of Alkyl Radicals. Part III.*[1] *n-Butyl Radicals from the Photolysis of n-Valeraldehyde.*

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The photo-initiated chain decomposition of n-valeraldehyde, alone and when mixed with ethylene or n-butyraldehyde, has been studied. A mechanism that accounts for the rates of formation of most of the principal products has been constructed. On the assumption that the rate constant for the combination of n-butyl radicals is given by log $k = 14$, the following Arrhenius parameters of the principal rate-determining reactions have been found:

	log A	E
$2C_4H_9 \longrightarrow C_4H_8 + C_4H_{10}$	14·6	1·3
$C_4H_9 + C_4H_9{\cdot}CHO \longrightarrow C_4H_{10} + C_4H_9{\cdot}CO$	10·9	5·4
$C_4H_9 \longrightarrow C_2H_5 + C_2H_4$	11·2	22·0
$C_4H_9 \longrightarrow CH_3 + C_3H_6$	12·1	27·1
$C_4H_9 + C_2H_4 \longrightarrow C_6H_{13}$	11·1	7·3

where k and A are in units of mole^{-1} cm.^{3} sec.$^{-1}$ or sec.$^{-1}$, and E is in kcal. mole^{-1}. The rate constant for the combination of n-butyl and n-propyl radicals is twice the geometric mean of the constants for the auto-combinations.

THE first two papers in this series[1] described the reactions of n-propyl and isopropyl radicals produced in the photo-initiated chain decompositions of n-butyraldehyde and isobutyraldehyde. This paper deals with a parallel study of n-butyl radicals from n-valeraldehyde. The photolysis of this aldehyde has not previously been studied in detail. Furthermore, little was known about the reactions of n-butyl radicals because no suitable sources had been found. Calvert has studied the disproportionation reactions of the other butyl radicals[2] and the photolysis of α-methylbutyraldehyde.[3]

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[1] Parts I and II, Kerr and Trotman-Dickenson, *Trans. Faraday Soc.*, 1959, **55**, 572, 921.

[2] Kraus and Calvert, *J. Amer. Chem. Soc.*, 1957, **79**, 5921.

[3] Gruver and Calvert, *J. Amer. Chem. Soc.*, 1956, **78**, 5208; 1958, **80**, 3524.

EXPERIMENTAL

The apparatus and procedure were substantially the same as those previously employed.[1] The chromatographic column A (150 cm.) was packed with powdered firebrick (25—52 mesh)–10% of dimethyl phthalate; it was used to separate all the hydrocarbon products. Column B (150 cm.) was packed with activated alumina (30–52 mesh) impregnated with 1% of squalane. The flow rate of the carrier gas (hydrogen) was 25 cm.^{3} min.$^{-1}$.

Photolysis was by light from a 125 w medium-pressure mercury arc. The amounts of n-octane produced were always small and any considerable reduction in these quantities resulted in reduction in the accuracy with which they could be estimated. Accordingly, the lamp was placed as close as possible (about 20 cm.) to the front face of the reaction cell. No filter was used, so the radicals initially formed may have carried over variable amounts of energy from the primary act. At the higher temperatures, most of the radicals were formed by the decomposition of the valeryl radicals so that the primary act was unimportant. No workers have reported that the behaviour of alkyl radicals formed in the photolysis of ketones above 100° depends upon the wavelength of the light. It is therefore unlikely that the present results would be altered by the presence of a filter.

The commercial n-valeraldehyde was shown to be pure by gas chromatography and by the nature of the products formed on photolysis. The range of pressures of the aldehyde that could be studied was limited by its low volatility. At low temperatures the aldehyde was admitted to the reaction vessel some time before the light-shutter was removed. At high temperatures the addition was very rapid and light was admitted almost simultaneously. This precaution kept the amount of thermal decomposition very low.

RESULTS AND DISCUSSION

Twenty-two runs were carried out between 61° and 416° c. The products were analysed for carbon monoxide, hydrogen, methane, ethane, ethylene, propane, propylene, n-butane, but-1-ene, and n-octane. The results are given in Table 1, and show that all the reactions listed below occur. Deductions can be made about the rate constants of the reactions distinguished by a simple number. Other reactions certainly occur, as will be indicated in the discussion, but little or nothing can be said about their rate constants. All reaction systems involving large radicals and molecules are complicated; this photolysis is no exception. Additional experiments with isotopic tracers and in the presence of substances such as nitric oxide and iodine are needed to elucidate fully the reaction scheme.

$$C_4H_9{\cdot}CHO + h\nu \longrightarrow C_4H_9 + HCO \quad \ldots\ldots \quad (a)$$

$$HCO \longrightarrow H + CO \quad \ldots\ldots \quad (b)$$

$$2C_4H_9 \xrightarrow{k_1} C_8H_{18} \quad \ldots\ldots \quad (1)$$

$$2C_4H_9 \xrightarrow{k_2} C_4H_8 + C_4H_{10} \quad \ldots\ldots \quad (2)$$

$$C_4H_9 + C_4H_9{\cdot}CHO \xrightarrow{k_3} C_4H_{10} + C_4H_9{\cdot}CO \quad \ldots\ldots \quad (3)$$

$$C_4H_9{\cdot}CO \longrightarrow C_4H_9 + CO \quad \ldots\ldots \quad (3a)$$

$$C_4H_9 \xrightarrow{k_4} C_2H_5 + C_2H_4 \quad \ldots\ldots \quad (4)$$

$$C_2H_5 + C_4H_9{\cdot}CHO \longrightarrow C_2H_6 + C_4H_9{\cdot}CO \quad \ldots\ldots \quad (4a)$$

$$C_4H_9 \xrightarrow{k_5} CH_3 + C_3H_6 \quad \ldots\ldots \quad (5)$$

$$CH_3 + C_4H_9{\cdot}CHO \longrightarrow CH_4 + C_4H_9{\cdot}CO \quad \ldots\ldots \quad (5a)$$

$$CH_3 + C_2H_5 \longrightarrow C_3H_8 \quad \ldots\ldots \quad (5b)$$

The Photolytic Act (*Reaction*).—This would be most convenient as a source of *n*-butyl radicals if all the molecules photolysed yielded a butyl radical. At 60° the yields of but-1-ene, n-butane, and n-octane indicate that about one-third of the molecules that produce carbon monoxide on photolysis yield a butyl radical; photolysis also yields methyl and ethyl radicals, ethylene, and rather large amounts of propene (up to 80% of the amount of carbon monoxide). The amount of propene is high by comparison with the

TABLE 1. *The photolysis of n-valeraldehyde.*

No.	Temp. (K)	Time (sec.)	[Ald]	CO	CH_4	C_2H_4	C_2H_6	C_3H_6	C_3H_8	C_4H_8	C_4H_{10}	C_8H_{18}
1	334°	12,600	1·06	13·0	0·780a	0·709	0·399	12·05	0·821	0·421	2·90	0·740
2	354	10,800	1·12	12·6	0·399a	0·941	0·476	10·5	0·859	0·314	3·19	0·524
3	371	10,800	1·10	13·2	1·31	0·811	0·418	10·5	0·655	0·340	3·98	0·439
4	376	10,800	0·830	12·5	0·554a	0·649	0·319	a.f.	0·838	0·456	a.f.	0·665
5	384	10,800	0·851	13·0	0·802	0·481	0·356	9·48	0·591	0·371	3·99	0·501
6	401	9000	1·02	19·1	0·336a	0·930	0·735	10·9	1·10	0·270	5·90	a.f.
7	406	7800	0·941	12·7	1·01	0·362	0·188	5·79	0·326	a.f.	3·48	0·188
8	421	7200	0·822	15·4	0·294a	0·549	0·392	9·00	0·675	0·581	6·55	0·660
9	443	7200	0·855	22·3	0·981	0·565	0·541	7·65	0·887	0·318	9·06	0·353
10	449	7200	0·729	20·6	0·704a	0·408	0·353	7·29	0·667	0·212	7·85	a.f.
11	477	6000	0·660	21·0	0·485a	0·848	1·25	4·90	1·69	0·254	8·39	0·245
12	502	5400	0·716	36·1	1·14	2·30	2·60	8·16	1·88	0·429	20·3	0·392
13	526	4680	0·518	35·6	0·79	5·64	5·41	7·36	1·51	u	12·4	0·300(X)
14	544	2400	0·676	49·4	1·20	9·90	10·0	6·60	3·58	u	16·9	0·237(X)
15	571	1800	0·654	60·3	2·61	24·6	25·6	8·80	4·52	u	16·6	0·154(X)
16	578	1320	0·705	80·0	4·11	40·7	41·0	10·0	5·16	u	20·4	0·175(X)
17	595	1020	0·635	130	a.f.	64·4	65·6	16·6	6·65	u	26·9	0·298(X)
18	609	720	0·636	137	8·51	a.f.	a.f.	14·6	6·74	u	16·8	0·092(X)
19	629	600	0·601	208	15·1	103	103	24·4	7·72	u	17·0	0·080(X)
20	645	480	0·620	216	20·2	a.f.	a.f.	29·4	5·88	u	17·7	0·065(X)
21	664	360	0·650	254	33·8	170	172	44·0	10·0	u	18·1	0·049(X)
22	689	240	0·575	447	57·7	373	a.f.	64·3	4·72	u	18·3	0·046(X)

No.	k_2/k_1	(C_4H_{10}–C_4H_8)	$k_3/k_1^{\frac{1}{2}}$	C_2H_4 *	$k_4/k_1^{\frac{1}{2}}$	C_2H_6 *	$k_4'/k_1^{\frac{1}{2}}$	C_3H_6 *	$k_5/k_1^{\frac{1}{2}}$	CH_4 *	$k_5'/k_1^{\frac{1}{2}}$
1	0·569	2·48	2·72	—	—	—	—	—	—	—	—
2	0·600	2·88	3·55	—	—	—	—	—	—	—	—
3	0·775	3·64	5·00	—	—	—	—	—	—	—	—
4	0·686	—	—	—	—	—	—	—	—	—	—
5	0·741	3·62	6·01	—	—	—	—	—	—	—	—
6	—	—	—	—	—	—	—	—	—	—	—
7	—	3·33	10·0	—	—	—	—	—	—	—	—
8	0·881	5·97	8·94	—	—	—	—	—	—	—	—
9	0·902	8·74	17·2	—	—	—	—	—	—	—	—
10	—	—	—	—	—	—	—	—	—	—	—
11	1·04	8·14	24·9	0·378	0·764	0·91	1·84	—	—	—	—
12	1·09	19·9	44·4	1·79	2·86	2·26	3·61	—	—	—	—
13	—	—	—	5·27	9·63	5·16	9·42	—	—	—	—
14	—	—	—	9·42	19·3	9·68	19·8	—	—	—	—
15	—	—	—	24·1	61·4	25·3	64·4	1·93	4·91	1·73	4·40
16	—	—	—	40·4	96·4	40·7	97·1	2·60	6·21	3·15	7·52
17	—	—	—	63·9	117	65·2	119	9·95	18·2	—	—
18	—	—	—	—	—	—	—	7·93	26·1	7·65	25·2
19	—	—	—	102·6	363	102·7	363	18·1	64·0	14·3	50·6
20	—	—	—	—	—	—	—	22·9	89·9	19·4	76·2
21	—	—	—	171·5	773	169·7	765	37·2	168	32·9	148
22	—	—	—	—	—	372·8	1740	58·3	272	56·9	266

Rates of formation of products are given as 10^{-12} mole cm.$^{-3}$ sec.$^{-1}$.
[Ald] is the mean concentration of aldehyde, in 10^{-6} mole cm.$^{-3}$.
$k_3/k_1^{\frac{1}{2}}$ is in mole$^{-\frac{1}{2}}$ cm.$^{\frac{3}{2}}$ sec.$^{-\frac{1}{2}}$; $k_4/k_1^{\frac{1}{2}}$ and $k_5/k_1^{\frac{1}{2}}$ are in 10^6 mole$^{\frac{1}{2}}$ cm.$^{-\frac{3}{2}}$ sec.$^{-\frac{1}{2}}$.
* indicates rate of formation of product corrected for the primary photolytic act.
(X) indicates a calculated value. a.f. = analytical failure.
u = not detectable on the chromatogram.
a = unreliable methane analysis, owing to over-oxidation.

yield of ethylene from the analogous type 2 decomposition of n-butyraldehyde[3] and α-methyl butyraldehyde.[4] On the other hand, considerable quantities of propene are formed in the photolysis of isovaleraldehyde.[5]

The Combination of n-Butyl Radicals (*Reaction* 1).—This is the source of n-octane, formed according to the rate (*R*) equation, $R_{C_8H_{18}} = k_1\,[C_4H_9]^2$.

Experimental investigations of the rate constant of the combination of butyl radicals have not been reported; accordingly a conventional rate constant, log k_1 (mole^{-1} cm.^{3} sec.$^{-1}$) = 14, has been assumed for the purposes of presenting the results.

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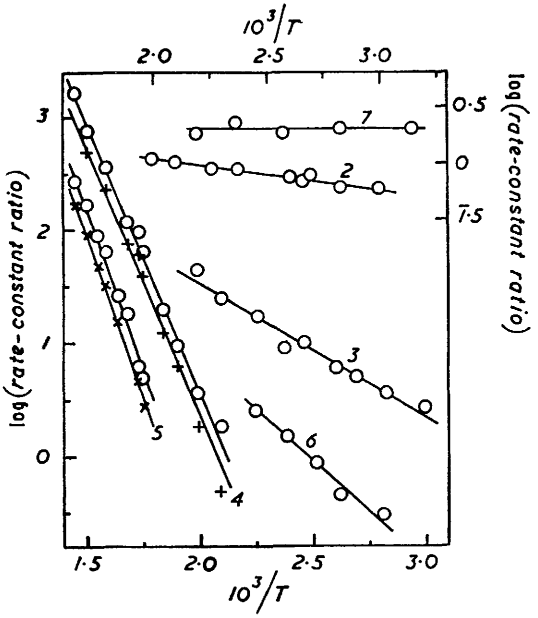
[4] Blacet and Calvert, *J. Amer. Chem. Soc.*, 1951, **73**, 661.
[5] Bamford and Norrish, *J.*, 1935, 1504.

The Disproportionation of n-Butyl Radicals (*Reaction* 2).—Nine runs that provide direct information on k_2 were carried out between 61° and 229°, with mean aldehyde concentrations between 0·66 and 1·12 μmole cm.$^{-3}$. The number of radicals disproportionating was taken as being twice the quantity of butene found at the end of the run. Hence

Arrhenius plots for the reactions of n-butyl: 2, *disproportionation,* k_2/k_1; 7, *cross-combination,* $k_7/(k_1k_8)^{\frac{1}{2}}$ (*the scales at the top right hand corner refer to these plots*); 3, *hydrogen abstraction,* $k_3/k_1^{\frac{1}{2}}$ (*mole*$^{-\frac{1}{2}}$ *cm.*$^{\frac{3}{2}}$ *sec.*$^{-\frac{1}{2}}$); 4, *decomposition to ethyl and ethylene,* $10^6k_4/k_1^{\frac{1}{2}}$ (*mole*$^{\frac{1}{2}}$ *cm.*$^{-\frac{3}{2}}$ *sec.*$^{-\frac{1}{2}}$), *open circles, results based on ethane, crosses, results based on ethylene;* 5, *decomposition to methyl and propene,* $10^6k_5/k_1^{\frac{1}{2}}$ (*mole*$^{\frac{1}{2}}$ *cm.*$^{-\frac{3}{2}}$ *sec.*$^{-\frac{1}{2}}$), *open circles, results based on methane, crosses, results based on propene;* 6, *addition to ethylene,* $k_6/k_1^{\frac{1}{2}}$ (*mole*$^{-\frac{1}{2}}$ *cm.*$^{\frac{3}{2}}$ *sec.*$^{-\frac{1}{2}}$). *The crosses drawn for curves* 4 *and* 5 *have all been displaced* 0·2 *unit downwards. The lower curves* 4 *and* 5 *were obtained by displacing the upper lines* 0·2 *unit downwards.*



$k_2/k_1 = R_{C_4H_8}/R_{C_8H_{18}}$. Values of log (k_2/k_1) are plotted against the reciprocal temperature in Fig. 1. As $(E_2 - E_1) = 1{\cdot}3$ kcal. mole^{-1} and $A_2 = 4A_1$,

$$\log k_2\ (\text{mole}^{-1}\ \text{cm.}^3\ \text{sec.}^{-1}) = 14{\cdot}6 - (1300/2{\cdot}303\boldsymbol{R}T)$$

This result differs considerably from the value of 0·5 for k_2/k_1 derived from studies of the photolysis of di-n-butylmercury at 320°.[6] No complete kinetic analysis of that system was made, so it is difficult to know how much reliance should be placed on the results. Furthermore, there is evidence that radicals formed by the photolysis of mercury alkyls are abnormally susceptible to disproportionation unless they are deactivated by numerous collisions with inert molecules.[7] A more weighty reason for doubting our findings is the magnitude of the temperature coefficient. At least six pairs of combination–disproportionations of alkyl radicals in the gas phase have now been reliably studied without any measurable temperature coefficient being found. Despite this fact we believe the temperature coefficient to be real. The general method employed here gave results that were in excellent agreement with those obtained by photolysis of ketones for ethyl, n-propyl, and isopropyl radicals.[8] Furthermore, it is

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[6] Moore and Wall, *J. Chem. Phys.*, 1949, **17**, 1325.

[7] Bradley, Melville, and Robb, *Proc. Roy. Soc.*, 1956, *A*, **236**, 318.

[8] This work, Parts I and II, and unpublished work with propionaldehyde.

difficult to see how n-octane could be formed except by the combination of radicals. Butene might have been produced in the primary photolytic act as well as by disproportionation, but if it was, then a negative temperature coefficient would have been expected for k_2/k_1. If butene were formed in the decomposition of an aldehydic radical produced by hydrogen abstraction, a markedly curved Arrhenius plot would be expected.

The value of k_2/k_1 at 100°, 0·70, is significantly lower than the value of 0·9 predicted by Kraus and Calvert [2] on the basis of the number of hydrogen atoms available for attack in the disproportionation of the butenes.

The Abstraction of a Hydrogen Atom from n-Valeraldehyde (*Reaction* 3).—The rate of attack of a n-butyl radical on the aldehydic hydrogen in n-valeraldehyde has been computed on the assumption that all the butane that is not formed in disproportionation comes from this attack. Hence we can write:

$$k_3/k_1^{\frac{1}{2}} = (R_{C_4H_{10}} - R_{C_4H_8})/R_{C_8H_{18}}^{\frac{1}{2}}\,[C_4H_9\cdot CHO]$$

In this expression $[C_4H_9\cdot CHO]$ refers to the mean concentration of the aldehyde. The Arrhenius plot shown in the Figure for results obtained between 61° and 229° and with 0·66 to 1·12 μmole cm.$^{-3}$ of aldehyde yields:

$$\log k_3\ (\text{mole}^{-1}\ \text{cm.}^3\ \text{sec.}^{-1}) = 10{\cdot}9 - (5400/2{\cdot}303\boldsymbol{R}T)$$

By this method k_3 is clearly overestimated because some butane must be formed by attack on the alkyl group in the aldehyde; the error introduced is probably small. It is unfortunate that attack on the alkyl group does not yield a distinctive product by which the rate of attack could be directly estimated. Results with n-butyraldehyde indicate that allowance for this secondary source of butane would only reduce log A_3 by 0·05. The effect on E_3 must be negligible. The simplification tends to favour an erroneously high value of E_3. The apparently low value of E_3 can be ascribed either to the high reactivity of n-butyl or to E_1 being greater than zero. It may be noted that if the rate constant for the combination of two s-butyl radicals is 10^{14} mole^{-1} cm.^{3} sec.$^{-1}$, the rate constant for the attack of s-butyl on α-methylbutyraldehyde is given by [3]

$$\log k = 10{\cdot}5 - (4900/2{\cdot}303\boldsymbol{R}T)$$

The scatter of the experimental points was considerable, and the low activation energy depends largely on the weight given to one point.

The Decomposition of n-Butyl to Ethylene (*Reaction* 4).—The decomposition of n-butyl radicals to ethyl radicals and ethylene can be followed by determining either the ethylene or the ethane formed; both methods have been employed. We can therefore write:

$$k_4/k_1^{\frac{1}{2}} = R_{C_2H_4}/R_{C_8H_{18}}^{\frac{1}{2}} = R_{C_2H_6}/R_{C_8H_{18}}^{\frac{1}{2}}$$

The corrections that had to be applied for the amounts of ethane and ethylene formed at low temperature were very small and made little difference to the final result. At most temperatures the amount of n-octane formed was so low that it could not be measured, it was estimated from the rate of formation of butane. Ten successful runs were carried out between 204° and 416° in which the mean aldehyde concentration was kept constant at about 0·63 μmole cm.$^{-3}$. Arrhenius plots for the rate constants obtained from both sets of measurements are shown in the Figure. The remarkably good agreement has been shown by displacing the points derived from the measurements of ethylene by 0·2 log units. The line drawn through the ethane points has been similarly displaced. Therefore, log k_4 (sec.$^{-1}$) = 11·2 − (22,000/2·303$\boldsymbol{R}T$).

The Decomposition of n-Butyl to Propene (*Reaction* 5).—The decomposition of n-butyl radicals to methyl radicals and propene can be similarly followed by determining either the methane or the propene formed, and hence equations written for k_5. The corrections that had to be applied to the figures for the rate of formation of propene, to allow for the formation of the propene that was presumed to originate in an initial photolytic decomposition, were considerable at the lower temperatures. It is all the more gratifying that the figures for methane and propene balance so well. This is shown in the Arrhenius plot in the Figure which shows the results from eight runs, all of which were used in the estimation of k_5. We find that

$$\log k_5 \text{ (sec.}^{-1}) = 12{\cdot}1 - (27{,}100/2{\cdot}303\boldsymbol{R}T)$$

The comparatively large rate constant for reaction 5 is surprising because it was previously supposed that n-butyl did not yield methyl radicals and propene. The work of Frey and Hepp[9] on the pyrolysis of di-n-butylmercury seemed fairly conclusive. No satisfactory explanation can be given for the absence of propene from their products. McNesby, Drew, and Gordon[10] found that the propene occurring among the products of the decomposition of butyl radicals formed by the reaction of methyl radicals with 2,2,3,3-tetradeuterobutane always contained three deuterium atoms. They supposed that this could only come from the decomposition of $CH_3{\cdot}CD{\cdot}CD_2{-}CH_3$ and that $CH_2{\cdot}CD_2{\cdot}CD_2{\cdot}CH_3$ could only yield $CH_2{\cdot}CD{\cdot}CD_3$ and CH_3 by the transfer of a deuterium atom between adjacent carbon atoms. It is, however, possible that a four-centre activated complex (involving carbon atoms 1 and 3) may be involved in the transfer of the deuterium atom, which would yield CH_2D and $CD_2{\cdot}CD{\cdot}CH_3$. McNesby and Gordon wrote when no certain example of alkyl radical isomerisation was known. Since then it has been shown[1,11] that the isopropyl radical will decompose to a methyl radical and ethylene.

Bywater and Steacie[12] studied the mercury-photosensitised decomposition of n-butane at high temperatures. The rate constants, A factors, and activation energies that can be deduced[13] from their work agree well with those reported here. It is, however, likely that they were dealing largely with s-butyl radicals.

At high temperatures propane was formed in amounts corresponding to about 5% of the carbon monoxide. Some may have been the product of the combination of methyl and ethyl radicals but it seems unlikely that it can all be attributed to this reaction. The mechanism of high-temperature reaction is uncertain to this extent.

The Addition of n-Butyl to Ethylene (*Reaction* 6).—When ethylene is added to the n-valeraldehyde, reaction (6) takes place:

$$C_4H_9 + C_2H_4 = C_6H_{13} \quad . \; . \; . \; . \; . \; . \; . \; . \; . \quad (6)$$

This is followed by

$$C_6H_{13} + C_4H_9{\cdot}CHO = C_6H_{14} + C_4H_9{\cdot}CO \quad . \; . \; . \; . \; . \quad (6a)$$

which accounts for about 80% of the hexyl radicals when the concentration of the ethylene is 3·6 μmole cm.$^{-3}$ and that of the aldehyde is 1·2 μmole cm.$^{-3}$. Some 10% of the hexyl radicals add a further ethylene, forming octyl radicals which eventually form n-octane. Because of these reactions the concentration of n-butyl radicals must be deduced from the butane formed. The rate of formation of n-octane is then deduced from the rate constants that have previously been determined. Hence we can write

$$k_6/k_1^{\frac{1}{2}} = R(\text{hexyl products})/R_{C_8H_{18}}[C_2H_4]$$

The Arrhenius plot for this rate-constant ratio is shown in the Figure from which

$$\log k_6 \text{ (mole}^{-1}\text{ cm.}^3\text{ sec.}^{-1}) = 11{\cdot}1 - (7300/2{\cdot}303\boldsymbol{R}T).$$

The Combination of n-Butyl and n-Propyl (*Reaction* 7).—When a mixture of n-butyraldehyde (0·6 to 1·0 μmole cm.$^{-3}$) and n-valeraldehyde (0·7 to 1·2 μmole cm.$^{-3}$) was

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[9] Frey and Hepp, *J. Amer. Chem. Soc.*, 1933, **55**, 3357.

[10] McNesby, Drew, and Gordon, *J. Chem. Phys.*, 1956, **24**, 1260.

[11] Heller and Gordon, *J. Phys. Chem.*, 1958, **62**, 709.

[12] Bywater and Steacie, *J. Chem. Phys.*, 1951, **19**, 172.

[13] Trotman-Dickenson, "Gas Kinetics," Butterworths, London, 1955, p. 303.

photolysed, n-hexane, n-heptane, and n-octane were formed, presumably by reactions (1), (7), and (8):

$$C_3H_7 + C_4H_9 = C_7H_{16} \quad \ldots \ldots \ldots \quad (7)$$

$$2C_3H_7 = C_6H_{14} \quad \ldots \ldots \ldots \quad (8)$$

Hence $$k_7/(k_1k_8)^{\frac{1}{2}} = R_{C_7H_{16}}/(R_{C_6H_{14}}R_{C_8H_{18}})^{\frac{1}{2}}$$

The results plotted in the Figure show that, between 45° and 184°, $k_7/(k_1k_8)^{\frac{1}{2}} = 2{\cdot}0 \pm 0{\cdot}2$, and is independent of temperature. This finding, taken together with the information on other cross-combinations,[14] is good evidence that none of the combinations has an activation energy. In a single run with isobutyraldehyde a ratio of 2·16 was found for n-butyl and isopropyl radicals.

The Energetics of the Radical Decompositions.—The following equations govern the energetics of the decomposition of n-butyl radicals to ethyl and ethylene:

$$D(C_2H_5\text{–}CH_2{\cdot}CH_2\text{–}) = \Delta H_f{}^\circ\,(C_2H_5) + \Delta H_f{}^\circ\,(C_2H_4) - \Delta H_f{}^\circ\,(\text{n-}C_4H_9)$$
$$= E_4 - E_{-4}$$

But $$\Delta H_f{}^\circ\,(\text{n-}C_4H_9) = \Delta H_f{}^\circ\,(C_4H_{10}) + D(C_4H_9\text{–}H) - \Delta H_f{}^\circ(H)$$

Therefore, $$E_4 - E_{-4} = \Delta H_f{}^\circ(C_2H_5) + \Delta H_f{}^\circ(C_2H_4) - \Delta H_f{}^\circ(C_4H_{10}) - D(C_4H_9\text{–}H) + \Delta H_f{}^\circ(H)$$

Substituting values, we have [15]

$$22 - E_{-4} = 25{\cdot}2 + 12{\cdot}5 + 30{\cdot}2 - D(C_4H_9\text{–}H) + 52$$

Therefore, $$D(C_4H_9\text{–}H) = E_{-4} + 98$$

E_{-4} is about 8 kcal. mole^{-1} if the combination of ethyl radicals has no activation energy.[16] This value is in good agreement with that which can be deduced from information on the addition of ethyl radicals to other olefins.[17] Hence $D(C_4H_9\text{–}H) \approx 106$ kcal. mole^{-1}. This value seems improbably high. The most likely cause of the discrepancy is the underestimation of E_4. The low value of A_4 lends support to this supposition. The value of k_4 obtained at about 300° is probably reliable.

It is not known if the overall decomposition (reaction 5) of n-butyl radicals into methyl radicals and propene occurs in one step in which the isomerisation and decomposition are simultaneous. Isomerisation may occur first and it may be the rate of this process that is measured. The isomerisation is exothermic and yields a s-butyl radical containing energy considerably in excess of the critical energy for decomposition. Unless it is deactivated by collision it will necessarily decompose. At the comparatively low pressures of our experiments few of the radicals are likely to be deactivated. An indication that isomerisation occurs first with a high activation energy can be seen in the work of Brinton [18] on the addition of methyl to ethylene. If decomposition and isomerisation of large radicals were simultaneous processes, the addition of small radicals to olefins and the isomerisation of the resultant large radical would also be simultaneous. Hence the addition of methyl radicals to ethylene could yield isopropyl as well as n-propyl radicals. Brinton found n-butane (from n-propyl plus methyl) in his products but no isobutane. There is therefore no evidence for isomerisation in this case.

Only if decomposition and isomerisation are simultaneous can the energetics of the processes be calculated. A treatment similar to that given above for equation (4) yields $D(C_4H_9\text{–}H) = E_{-5} + 92{\cdot}5$, or a value for the C–H bond of about 100 kcal. mole^{-1} which is reasonable, but for the reasons outlined above, little significance should be attached to this value.

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[14] Kerr and Trotman-Dickenson, *Chem. and Ind.*, 1959, 125.

[15] Ref. 13, p. 15.

[16] Kerr and Trotman-Dickenson, unpublished results.

[17] James and Steacie, *Proc. Roy. Soc.*, 1958, *A*, **244**, 297.

[18] Brinton, *J. Chem. Phys.*, 1958, **29**, 781.