THE REACTIONS OF ALKYL RADICALS

PART 2.—*s*-PROPYL RADICALS FROM THE PHOTOLYSIS OF *iso*BUTYRALDEHYDE

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The photo-initiated chain decomposition of *iso*butyraldehyde, alone and when mixed with ethylene or propionaldehyde, has been studied. A mechanism that accounts for the rates of formation of the principal products has been constructed. The amounts of hydrogen, carbon monoxide, methane, ethylene, propane, propylene and 2:3-dimethyl butane were determined in the runs with the pure aldehyde. On the basis of an assumed rate constant for the combination of *s*-propyl radicals, activation energies and *A* factors for disproportionation, hydrogen abstraction, addition to ethylene, and decomposition both to ethylene and propylene were obtained. The results are summarized and compared with similar results for *n*-propyl in table 1. The rate constant for the combination of ethyl and *s*-propyl is twice the geometric mean of the constants for the autocombinations.

The first paper in this series[1] described the reactions of *n*-propyl radicals produced in the photoinitiated chain decomposition of *n*-butyraldehyde. This paper deals with a parallel study of *s*-propyl radicals from *iso*butyraldehyde. More was previously known of these radicals because they can be cleanly produced by the photolysis of di-*iso*propyl ketone. They are also principally formed in the mercury-photosensitized addition of hydrogen to propylene and in the mercury-photosensitized decomposition of propane.

EXPERIMENTAL

The apparatus, the procedure, and many of the gases were the same as were employed in part 1. B.D.H. *iso*butyraldehyde was degassed before use. Gas chromatographic analysis showed it to be pure.

RESULTS AND DISCUSSION

Twenty-five runs were carried out in which the photo-initiated chain decomposition of *iso*butyraldehyde was studied between 20° and 501°C. The products were analyzed for carbon monoxide, hydrogen, methane, ethylene, propylene, propane and 2:3-dimethyl butane. No ethane was detected. The results, taken in conjunction with other work referred to later, indicate that all the following reactions take place to a measurable extent, though others cannot be definitely excluded.

$$(CH_3)_2CHCHO + h\nu \rightarrow C_3H_7 + CHO \qquad (a)$$
$$\rightarrow C_3H_8 + CO \qquad (b)$$
$$\rightarrow CH_3 + C_2H_4CHO \qquad (c)$$
$$2C_3H_7 = C_6H_{14} \qquad (1)$$
$$2C_3H_7 = C_3H_6 + C_3H_8 \qquad (2)$$
$$C_3H_7 + C_3H_7CHO = C_3H_8 + C_3H_7CO \qquad (3)$$
$$(CH_3)_2CHCO = (CH_3)_2CH + CO \qquad (3a)$$

$$C_3H_7 + (CH_3)_2CHCHO = C_3H_8 + CH_2(CH_3)CHCHO \tag{4}$$

$$CH_2(CH_3)CHCHO = C_3H_6 + HCO \tag{4\textit{a}}$$

$$HCO = H + CO \tag{4\textit{b}}$$

$$H + C_3H_7CHO = H_2 + C_4H_7O \tag{4\textit{c}}$$

$$HCO + C_3H_7CHO = H_2CO + C_4H_7O \tag{4\textit{d}}$$

$$C_3H_7 + (CH_3)_2CHCHO = C_3H_8 + (CH_3)_2CCHO \tag{5}$$

$$(CH_3)_2CCHO = C_2H_3CHO + CH_3 \tag{5\textit{a}}$$

$$CH_3 + C_3H_7CHO = CH_4 + C_4H_7O \tag{5\textit{b}}$$

$$(CH_3)_2CCHO \rightarrow \text{unidentified products} \tag{5\textit{c}}$$

$$C_3H_7 = CH_3 + C_2H_4 \tag{6}$$

$$C_3H_7 = H + C_3H_6. \tag{7}$$

THE PHOTOLYTIC ACT (*a*), (*b*), (*c*)

The most complete evidence on the nature of the photolytic act comes from the work of Blacet and Calvert.[2] They studied the products of the photolysis of the pure substance and in mixtures with iodine. With radiation of 2654 Å, approximately equal numbers of molecules react by (*a*) and (*b*), but only one-tenth the number react by (*c*). In the present work, very small quantities of methane were produced at low temperatures. Even below 60°C, considerable quantities of propane were evidently formed by the chain process. The majority of the radicals present must then have been formed by (3*a*) and have been in energetic equilibrium with their environment. At 410°C the quantum yield for the formation of carbon monoxide was at least twenty times its value at 20°C.

THE COMBINATION OF *S*-PROPYL (1)

No measurements of the rate of combination of *s*-propyl have been reported although it would seem easier to investigate the photolysis of di-*iso*propyl ketone than di-*n*-propyl ketone by the rotating sector method. In the absence of any experimental determination, a conventional rate constant,

$$\log k_1/\text{mole}^{-1}\ \text{cm}^3\ \text{sec}^{-1} = 14,$$

has been assumed for the purposes of presenting the results. E_1 has been taken as zero because it is convenient. It is likely that this activation energy may be 1-2 kcal mole^{-1}, but not more.

THE DISPROPORTIONATION OF *S*-PROPYL (2)

One molecule of propylene is formed for each pair of propyl radicals that disproportionate. At low temperatures propylene is apparently only formed in this way, therefore

$$k_2 = R_{C_3H_6}/[C_3H_7]^2,$$

where $R_{C_3H_6}$ is the rate of formation of propylene. But

$$k_1 = R_{C_6H_{14}}/[C_3H_7]^2.$$

Therefore

$$k_2/k_1 = R_{C_3H_6}/R_{C_6H_{14}}.$$

The values that have been obtained in this way between 20° and 261°C are plotted in fig. 1. The line may be represented by the equation,

$$\log k_2/\text{mole}^{-1}\ \text{cm}^3\ \text{sec}^{-1} = 13{\cdot}82.$$

This rate constant corresponds to a value of $k_2/k_1 = 0{\cdot}65$ that is independent of temperature and was found not to vary when the aldehyde concentration was altered by a factor of five and the intensity of the absorbed light by about the same ratio. The result is in excellent agreement with that (0·63) of Heller and Gordon[3] from the photolysis of di-*iso*propyl ketone. The agreement is less good with the earlier work of Blacet and Calvert[2] (0·5) and Durham and Steacie[4] (0·53 at 30°C; 0·36 at 121°C) who used the photolysis of *iso*butyraldehyde and azo*iso*propane respectively as sources. The rather less accurate result (approx. 0·6) that Chilton and Gowenlock[5] obtained from a study of the pyrolysis of di-*iso*propyl mercury between 225° and 441°C is in as good agreement as could be expected. On the other hand Bradley, Melville and Robb[6] found that *s*-propyl radicals produced in 92 % purity by the mercury photosensitized addition of hydrogen atoms to propylene yielded a disproportionation ratio of 1·05 at 25°C. The radicals may have contained appreciable excess energy because of their method of formation. At the moment it would seem that the lower values should be preferred.

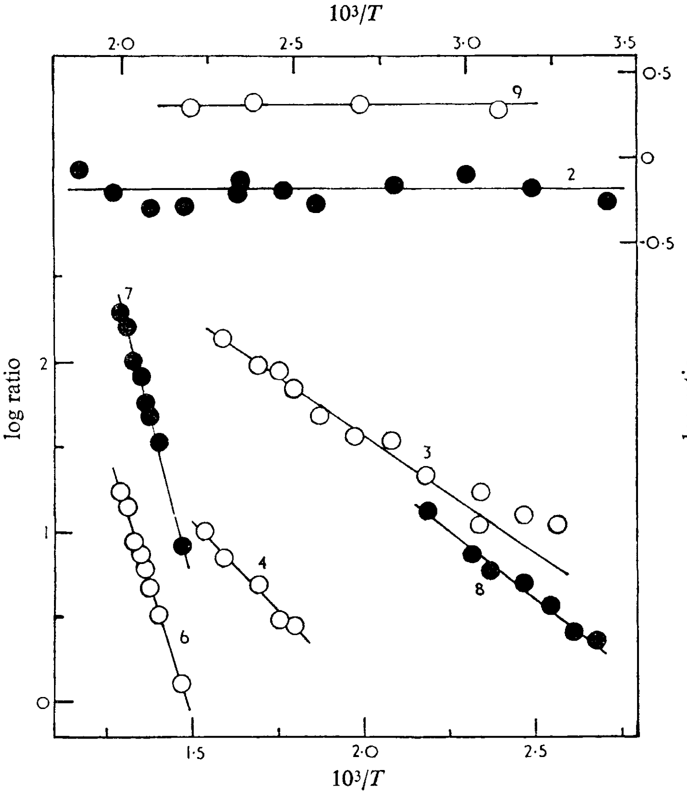

FIG. 1.—Arrhenius plots for the reactions of *s*-propyl: 2, disproportionation, k_2/k_1; 9, cross-combination, $k_9/(k_1k_{10})^{\frac{1}{2}}$, the scales at the top right-hand corner refer to these plots; 3, hydrogen abstraction, $(k_3/k_1^{\frac{1}{2}})$/mole$^{-\frac{1}{2}}$ cm$^{3/2}$ sec$^{-\frac{1}{2}}$; 4, hydrogen abstraction, $(k_4/k_1^{\frac{1}{2}})$/mole$^{-\frac{1}{2}}$ cm$^{3/2}$ sec$^{-\frac{1}{2}}$; 6, decomposition to methyl and ethylene, $10^6(k_6/k_1^{\frac{1}{2}})$/mole$^{\frac{1}{2}}$ cm$^{-3/2}$ sec$^{-\frac{1}{2}}$; 7, decomposition to propylene and a hydrogen atom, $10^6(k_7/k_1^{\frac{1}{2}})$/mole$^{\frac{1}{2}}$ cm$^{-3/2}$ sec$^{-\frac{1}{2}}$; 8, addition to ethylene, $(k_8/k_1^{\frac{1}{2}})$/mole$^{-\frac{1}{2}}$ cm$^{3/2}$ sec$^{-\frac{1}{2}}$.

THE ABSTRACTION OF HYDROGEN ATOMS FROM *iso*BUTYRALDEHYDE (4)

Above about 280°C the rate of production of propylene began to increase rapidly and in a way that could not be explained by disproportionation or by the decomposition of the *s*-propyl radical (reaction (7)). Reactions (4) and (4*a*) appear to account satisfactorily for the propylene in this photolysis; similar reactions were invoked in the discussion of the photolysis of *n*-butyraldehyde. We may write

$$C_3H_6\,(4a) = C_3H_6\,(\text{total}) - C_3H_6\,(2),$$

where $C_3H_6\,(4a)$ is the amount of propylene formed by reaction (4*a*). Since $C_3H_6\,(2) = 0{\cdot}65\ C_6H_{14}$, $C_3H_6\,(4a)$ may be found by subtraction. Then

$$R_{C_3H_8(4)} = R_{C_3H_6(4a)} = k_4[C_3H_7][C_3H_7CHO],$$

$$\therefore k_4/k_1^{\frac{1}{2}} = R_{C_3H_6(4a)}/R^{\frac{1}{2}}{}_{C_6H_{14}}[C_3H_7CHO].$$

The values of $k_4/k_1^{\frac{1}{2}}$ obtained in this way are plotted in fig. 1. From the Arrhenius plot between 283° and 377°C and for aldehyde concentrations between 0·52 and 1·20 μmole cm^{-3} we have

$$\log k_4/\text{mole}^{-1}\ \text{cm}^3\ \text{sec}^{-1} = 11{\cdot}2 - (9500/2{\cdot}303\ \boldsymbol{RT}).$$

It is reasonable to suppose that the reaction followed in this way is the removal of a primary hydrogen as this would give a radical likely to decompose into propylene. This result fits in reasonably with other work on the metathetical reactions of *s*-propyl which is summarized in table 1. The relative activation energy for the reaction again suggests that it is a primary hydrogen that is removed. Reaction (4*d*) must again [1] be postulated because of the marked deficiency of hydrogen (from 4*c*) in the products.

THE ABSTRACTION OF HYDROGEN ATOMS FROM *iso*BUTYRALDEHYDE (3)

The rate of attack of *s*-propyl on *iso*butyraldehyde has been taken as equal to

$$R_{C_3H_8} - R_{C_3H_6(4a)} - R_{C_3H_6(2)}.$$

This is in accord with the proposed mechanism if reaction (5) can be ignored. A comparison of the results in table 1 indicates that k_3 is probably ten or more times k_5. Furthermore, Birrell and Trotman-Dickenson [7] have shown that the butyraldehydes react with methyl at almost exactly the same rates as do acetaldehyde and propionaldehyde. It is therefore reasonable to conclude that the rate of attack on the aldehydic hydrogen is given by

$$k_3/k_1^{\frac{1}{2}} = (R_{C_3H_8} - R_{C_3H_6})/R^{\frac{1}{2}}{}_{C_6H_{14}}[C_3H_7CHO].$$

The Arrhenius plot shown in fig. 1 for the results obtained between 117° and 354°C and 2·0 and 0·4 μmole cm^{-3} mean concentration of aldehyde yields

$$\log k_3/\text{mole}^{-1}\ \text{cm}^3\ \text{sec}^{-1} = 11{\cdot}3 - (6300/2{\cdot}303\ \boldsymbol{RT}).$$

At a given temperature the change of a factor of four in the mean concentration of the aldehyde produced no change in the rate constant. Over the temperature range the quantum yield for the formation of carbon monoxide increased by a factor of approximately twelve.

Reaction (5) may be conveniently considered after reaction (6).

THE DECOMPOSITION OF *S*-PROPYL TO ETHYLENE (6)

When this work was begun it was thought that reaction (6) would not occur as information in the literature indicated that the parallel reactions of *s*-butyl are very slow.[8] It was found, however, that above 400°C considerable quantities of ethylene were formed and that the small amount of methane, that was produced at low temperatures, increased rapidly. These findings could be simply explained only if the *s*-propyl radical decomposed to methyl and ethylene. We may therefore write:

$$k_6/k_1^{\frac{1}{2}} = R_{C_2H_4}/R^{\frac{1}{2}}{}_{C_6H_{14}} = R_{CH_4}/R^{\frac{1}{2}}{}_{C_6H_{14}}.$$

The amounts of hexane were so small that they were estimated from measurements of $R_{C_3H_8}$ and the known relation between k_1, k_3 and k_4. Unfortunately, the rate of formation of methane, though rather irreproducible, is consistently about three times the rate of formation of ethylene. This discrepancy is too great to be attributed to the consumption of ethylene.

It is possible that the additional methyl leading to methane (reaction (5*b*)) is released by the decomposition of the aldehydic radical (5*a*). Since the ratio of $k_3 : k_4 : k_5$ will probably vary little between 400° and 500°C, the concentration of $(CH_3)_2CCHO$ could be proportional to the concentration of propyl. Furthermore since (5*a*) which yields acrolein is analogous to (6) it is likely that their activation energies are similar. The reaction sequence (5) may therefore be regarded as a reasonable explanation of the findings although there is little direct evidence for it. No useful estimate of k_5 can be made.

From the yield of ethylene we have

$$\log k_6/\text{sec}^{-1} = 10{\cdot}6 - (29500/2{\cdot}303\,\boldsymbol{R}T).$$

The points and the line corresponding to this equation are plotted in fig. 1. If the rate constant is calculated from the methane production we have

$$\log k_6/\text{sec}^{-1} = 10{\cdot}3 - (27100/2{\cdot}303\,\boldsymbol{R}T).$$

Some doubt is thrown on this interpretation by the work of Heller and Gordon [9] who find that *s*-propyl radicals from the photolysis of di-*iso*propyl ketone decompose with a rate constant given by

$$\log k_6/\text{sec}^{-1} = 12{\cdot}03 - (32500/2{\cdot}303\,\boldsymbol{R}T).$$

Their yields of ethylene and methane were excellently matched and their determination appears reliable. Their values of k_6 were three times those derived in this work from the ethylene analyses but agree well with those based on the methane. Fortunately, the uncertainties as to k_6 do not seriously affect the other conclusions of the present work because they relate only to runs above 400°C.

THE DECOMPOSITION OF *S*-PROPYL TO PROPYLENE (7)

Reaction (7) satisfactorily explains the steep rise in the rate of production of propylene between 400° and 500°C. We can write

$$k_7/k_1^{\frac{1}{2}} = (R_{C_3H_6} - R_{C_3H_6(4a)} - R_{C_3H_6(2)})/R^{\frac{1}{2}}_{C_6H_{14}}.$$

Again it is necessary to calculate the rate of formation of the hexane from that of the propane. The results obtained are plotted in fig. 1. The need to correct for the formation of propylene by two additional reactions does not introduce unreasonable errors as their contributions are small. The rate constant is given by

$$\log k_7/\text{sec}^{-1} = 13{\cdot}8 - (36900/2{\cdot}303\,\boldsymbol{R}T).$$

These rate constants are in excellent agreement with those of Heller and Gordon [9] given by

$$\log k_7/\text{sec}^{-1} = 13{\cdot}1 - (35000/2{\cdot}303\,\boldsymbol{R}T).$$

The Arrhenius parameters agree within the probable experimental errors.

Bywater and Steacie [10] measured k_6 and k_7 for the propyl radicals produced by the mercury-photosensitized decomposition of propane. At 440°C, about one-third of the steady-state concentration of propyl radicals were formed by the removal of a primary hydrogen atom from propane. The rate constants that can be derived from their results are given by [11]

$$\log k_6'/\text{sec}^{-1} = 9{\cdot}2 - (20000/2{\cdot}303\,\boldsymbol{R}T)$$

and

$$\log k_7'/\text{sec}^{-1} = 14{\cdot}6 - (38000/2{\cdot}303\,\boldsymbol{R}T).$$

The logarithms of their rate constants at 440°C ($\log k'_6 = 3\cdot1$, $\log k'_7 = 3\cdot0$) are reasonably in accord with those of Heller and Gordon for *s*-propyl ($\log k_6 = 2\cdot0$, $\log k_7 = 2\cdot5$) and ours for *s*-propyl ($\log k_6 = 1\cdot5$, $\log k_7 = 2\cdot5$) and for *n*-propyl [1] ($\log k^*_6 = 4\cdot0$, $\log k^*_7 = 2\cdot9$). It seems that most of Steacie and Bywater's products were formed by the decomposition of the *n*-propyl radicals.

The effect of the total pressure on the rate constants was not investigated.

THE ADDITION OF *S*-PROPYL TO ETHYLENE (8)

When ethylene is added to the *iso*butyraldehyde, reaction (8) takes place:

$$C_3H_7 + C_2H_4 = C_5H_{11}. \qquad (8)$$

It is followed by

$$C_5H_{11} + C_3H_7CHO = C_5H_{12} + C_4H_7O, \qquad (8a)$$

which accounts for about 85 % of the *iso*pentyl radicals if the concentration of the ethylene is double that of the aldehyde. About 10 % of the *iso*pentyl radicals add a further molecule of ethylene (8*b*)

$$C_5H_{11} + C_2H_4 = C_7H_{15} \qquad (8b)$$

and subsequently form 2-methyl hexane. A proportional correction of 1 % was made to allow for the *iso*pentyl radicals that ultimately form 2-methyl octane. The remaining *iso*pentyl radicals presumably dimerize, combine with propyl and disproportionate. The quantities of these products were small and no attempt was made to analyse for them. Their amount was estimated by making the assumption that *iso*pentyl radicals react like *s*-propyl radicals. An error of 10 % in this estimate probably leads to an error of only 1 % in k_8. Hence we can write

$$k_8/k_1^{\frac{1}{2}} = R\ (\text{pentyl products})/R^{\frac{1}{2}}_{C_6H_{14}}[C_2H_4].$$

The results obtained in this way are plotted in fig. 1. Hence

$$\log k_8/\text{mole}^{-1}\ \text{cm}^3\ \text{sec}^{-1} = 11\cdot4 - (6900/2\cdot303\ RT).$$

The Arrhenius parameters are very close to those for the similar reaction of *n*-propyl, given in table 1, but are lower than those for the addition of methyl to ethylene,[12]

$$\log k/\text{mole}^{-1}\ \text{cm}^3\ \text{sec}^{-1} = 12\cdot0 - (8660/2\cdot303\ RT).$$

THE COMBINATION OF ETHYL AND *S*-PROPYL (9)

When a mixture of propionaldehyde and *iso*butyraldehyde is photolysed *iso*pentane and *n*-butane are among the products. They are presumably formed by reactions (9) and (10),

$$C_2H_5 + C_3H_7 = C_5H_{12} \qquad (9)$$

$$2C_2H_5 = C_4H_{10}. \qquad (10)$$

Hence $$k_9/(k_1k_{10})^{\frac{1}{2}} = R_{C_5H_{12}}/(R_{C_4H_{10}}R_{C_6H_{14}})^{\frac{1}{2}}.$$

The results plotted in fig. 1 show that between 50° and 200°C, $k_9/(k_1k_{10})^{\frac{1}{2}} = 2\cdot04$ and is independent of temperature. A similar ratio may be derived from Wijnen's[13] determinations of the products formed in the photolysis of *iso*propyl propionate.[14]

THE ENERGETICS OF THE DECOMPOSITION OF *S*-PROPYL

The best available values of the Arrhenius parameters for the reactions of propyl radicals are listed in table 1. The most remarkable feature of the table is the similarity of the activation energies of the reactions of *n*- and *s*-propyl, for

TABLE 1.—THE REACTIONS OF PROPYL RADICALS

n-propyl reaction	log *A*	*E*	ref.	*s*-propyl reaction	log *A*	*E*	ref.
COMBINATION	14·0	0	*a*		14·0	0	*a*
DISPROPORTIONATION	13·2	0	1		13·82	0	*b*
H-TRANSFER REACTIONS							
$n\text{-}C_3H_7C\underline{H}O$	11·3	6·7	1	$iso C_3H_7C\underline{H}O$	11·3	6·3	*b*
$n\text{-}C_3\underline{H}_7CHO$	11·3	10·8	1	$(C\underline{H}_3)_2CHCHO$	11·2	9·5	*b*
$(n\text{-}C_3\underline{H}_7)_2CO$	10·7	6·5	*c*	$((CH_3)_2C\underline{D})_2CO$	11·1	9·3	9
				$((C\underline{H}_3)_2CD)_2CO$	11·8	11·7	9
				$((C\underline{H}_3)_2C\underline{H}N)_2$	10·4	6·5	4
DECOMPOSITION REACTIONS							
loss of CH_3	11·7	25·2	1	loss of CH_3	12·0	32·5	9
loss of H	13·6	35·0	1	loss of H	13·8	36·9	*b*
ADDITION REACTIONS							
to ethylene	10·9	6·5	1	to ethylene	11·4	6·9	*b*

All *A* factors are in mole^{-1} cm^3 sec^{-1} or sec^{-1}; *E* in kcal mole^{-1}.
(*a*) These values are assumed and are the basis of all the other rate constants.
(*b*) this work.
(*c*) Masson, *J. Amer. Chem. Soc.*, 1952, **74**, 4731.
The atoms underlined are those attacked in the transfer reactions.

it is generally believed that the strengths of the bonds broken when the radicals are formed from propane differ by three or more kcal mole^{-1}. The activation energies for the decompositions are most informative about the strengths of the bonds. In part 1 it was shown from simple thermodynamic arguments that

$$D(n\text{-}C_3H_7\text{—}H) = E^*_{-6} + 96{\cdot}6 \text{ and } E^*_{-7} + 99{\cdot}1,$$

where E^*_6 and E^*_7 are the activation energies for the decompositions of *n*-propyl into ethylene and propylene respectively (the negative sign denotes the reverse reaction throughout). In the same way it can be shown that

$$D(s\text{-}C_3H_7\text{—}H) = \mathrm{E}_{-6} + 89{\cdot}3 \text{ and } E_{-7} + 96{\cdot}8.$$

The incomplete evidence presently available indicates that the activation energies for the addition of hydrogen atoms and methyl radicals do not differ by more than 1 or 2 kcal mole^{-1}. Hence there is a discrepancy between the determinations of E_6 and E_7 of about 7 kcal mole^{-1}.

The value of $D(s\text{-}C_3H_7\text{—}H)$ that is currently accepted as the most probable is 94 kcal mole^{-1}. If E_{-6} is allotted the reasonable value of 8 kcal mole^{-1}, we have $D(s\text{-}C_3H_7\text{—}H) = 89{\cdot}3 + 8 = 97$ kcal mole^{-1} from the kinetic measurements. This value is, within the limits of the accumulated experimental errors, equal to that which is accepted. The agreement would be even more striking if the combination of *s*-propyl radicals has a small positive activation energy. For $D(s\text{-}C_3H_7\text{—}H) = 97 - \frac{1}{2}E_1$. A value of E_1 of a few kcal mole^{-1} would also bring E_8 more into line with the assumed value of E_{-6}. The agreement between the values for the strength of the C—H bond can, however, only be obtained on the assumption that the rearrangement of the incipient ethylidene in the activated complex has no activation energy.

The negligible energy barrier for the decomposition *s*-propyl to ethylene suggests that the configuration of the activated complex is very similar to that of the complex for the decomposition of *n*-propyl. Hence the activated complexes for the addition of methyl to ethylene must be nearly identical irrespective of whether *n*-propyl or *s*-propyl is ultimately formed. There are, indeed, some indications that the products of similar additions are formed in amounts determined more by the constants for the thermodynamic equilibria between the species than by kinetic considerations.

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