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Intramolecular Rearrangements of Hydrocarbon Radicals in the Gas Phase

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The review deals with the rearrangements of alkyl radicals occurring in various gas-phase processes. Intramolecular isomerisations involving the migration of a hydrogen atom with formation of three-, four-, five-, and six-membered transition states are examined. The possibility of the isomerisation of small alkyl radicals (ethyl and propyl radicals) and of the transfer of hydrogen to a neighbouring carbon atom in long-chain radicals is discussed. The process mechanism is considered. The bibliography includes 82 references.

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I. INTRODUCTION

Among reactions of free radicals, those involving their intramolecular isomerisation and leading to the migration of the free valence along the carbon skeleton of the species from one carbon atom to another are of special interest. Owing to isomerisation, the structure of the products of reactions involving free radicals can differ appreciably from that of the products which might have been expected in the absence of radical rearrangements. In many chain processes the isomerisation of the initially formed radicals can lead to the replacement of less active intermediate centres by more active ones. In polymerisation processes such rearrangements result in branching and cross-linking of the polymer chains.

The concept of radical isomerisation arose and began to be developed immediately after the discovery of free radicals and the elucidation of the role which they may play in various chemical reactions. In the 1940's–1950's, radical isomerisation was already adduced to explain experimental data for the thermal decomposition[1,2], isomerisation[3], oxidation[4-6], and other reactions[7,8] of organic compounds involving free radicals. However, one should note that at that time there was in fact no proof of the reality of processes of this kind.

This deficiency was eliminated to a considerable degree in the 1960's when studies on radical isomerisation were directed to the identification of radical centres. The first quantitative data for the kinetic characteristics of isomerisation processes have now also been obtained. In thermal or photolytic decomposition of various organic compounds, two or more isomeric radicals are formed via almost equally probable independent pathways and even the identification of the radicals and the use of tracer atoms do not always make it possible to state unambiguously whether radical rearrangements occur in the system. The fairly frequent formation in the system of structurally isomeric radicals can be explained by a sequence of bimolecular radical substitution, addition, and decomposition reactions without resorting to the hypothesis of radical isomerisation. Therefore numerous contradictory data and conclusions concerning the possible isomerisation of alkyl radicals by the migration of hydrogen atoms have accumulated in the literature dealing with gas-phase free-radical processes.

The present review is concerned with rearrangements of alkyl radicals in the gas phase. The review literature on this question is scanty. We can only point to one review in Czech[9] and a brief description of gas-phase radical rearrangements in monographs by Semenov[10], Pryor[11], Magaril[12], and Freidlina et al.[13] The well tested structural chemical principle of 1 – 2, 1 – 3, 1 – 4, 1 – 5, ... migrations of hydrogen atoms has been adopted in the present review for the classification of rearrangements. The numerical values indicate the relative positions of two rearrangement centres. However, wherever convenient, we have employed the approach of Rabinovitch and coworkers[14], designating the hydrogen atom shift as an *Nab* process, where *N* is the number of units in the ring of the cyclic transition state equal to 3, 4, 5, ..., *a* = *p*, *s*, or *t* refers to primary, secondary or tertiary C – H bonds undergoing dissociation, and *b* = *p*, *s*, or *t* refers to C – H bonds being formed.

Thus the isomerisation

$$CH_3-CH_2-CH_2-CH_2-\dot{C}H-CH_3 \rightarrow \dot{C}H_2-CH_2-CH_2-CH_2-CH_2-CH_3$$

will be designated as a 6*ps* reaction, which corresponds to a 1 – 5 migration of hydrogen according to the first classification. The Rabinovitch notation has the advantage that it reflects two important factors responsible for the occurrence of the rearrangement: the ring size of the transition state and the thermochemistry of the process, i.e. the conversion of less stable radicals into more stable radicals (the conversion of a primary into a secondary or tertiary radical) or conversely.

Intramolecular rearrangements of radicals are usually regarded as reactions of the radical with itself. Accordingly, the present review deals with intramolecular substitution reactions of alkyl radicals which can be represented schematically in the following way:

$$R-\dot{C}H-(CH_2)_n-\overset{H}{\underset{|}{C}}H-R' \rightarrow R-\overset{H}{\underset{|}{C}}H-(CH_2)_n-\dot{C}H-R',$$

where R, R′ is either a hydrogen atom or a hydrocarbon group.

II. 1 – 2 MIGRATION OF A HYDROGEN ATOM

Contradictory views have been expressed in the literature concerning the possibility that alkyl radicals can rearrange by the transfer of a hydrogen atom from a carbon atom adjoining the atom with an unpaired electron.

In order to account for the reaction products, many investigators had to resort to the hypothesis of 1 — 2 migration of a hydrogen atom; however, no one has succeeded in justifying rigorously a rearrangement of this type.

Glazebrook and Pearson[1] investigated the photolysis of di-isopropyl ketone, trapping the radicals formed with metallic mercury. When mercury iodide was added to the system, *n*-propylmercury iodide was obtained unexpectedly. This led the investigators to the conclusion that the isopropyl radicals formed in the primary photolytic step isomerise via a 3*ps* reaction into n-propyl radicals, the isomerisation probably occurring at the instant of the combination of the radical with mercury, since in the absence of the latter the rearrangement does not occur:

$$CH_3\dot{C}HCH_3 \rightarrow \dot{C}H_2CH_2CH_3 . \qquad (1)$$

This conclusion was questioned by Kharasch and coworkers[15,16], who investigated the thermal decomposition of n-propyl and isopropyl peroxides in carbon tetrachloride but failed to detect rearrangements of the alkyl radicals formed and concluded that there is no isomerisation in the gas-phase reactions either.

The decomposition of alkyl radicals is known to involve bonds in the β-position relative to the free valence[17] (the β-rule). In the presence of radical isomerisation, apparent deviations from this rule should be observed. Thus in the decomposition of isopropyl radicals, ethylene and a methyl radical should be formed, in the decomposition of n-butyl radicals—a methyl radical and propene, etc. The detection in the system of products of such "anomalous" decomposition might constitute serious evidence in support of the occurrence of radical rearrangements in the system.

Heller and Gordon[18] studied the photolysis of [D_2]di-isopropyl ketone at temperatures in the range 200 — 500°C and pressures of 14 — 16 mmHg. In the high-temperature range (407 — 504°C), they detected ethylene and methane in proportions close to 1 : 1. They suggested that under these conditions the anomalous decomposition of the isopropyl radical

$$CH_3\dot{C}DCH_3 \rightarrow CH_3CDH\dot{C}H_2 \rightarrow CH_2{=}CHD + \dot{C}H_3 \qquad (2)$$

plays an important role.

The presence in the system of n-propyl radicals is also indicated by the appearance on the chromatogram of a peak corresponding to 2-methylpentane, which is a product resulting from the combination of n-propyl and isopropyl radicals. The formation of the n-propyl radical via other pathways, namely by the attachment of H· to propene or the intermolecular isomerisation

$$CH_3\dot{C}DCH_3 + CH_3CH_2CH_3 \rightarrow CH_3CDHCH_3 + CH_3\dot{C}H_2CH_3$$

and "atomic cracking", did not occur under these conditions. If reaction (2) proceeds via two stages (rearrangement and decomposition), then, according to the authors, isomerisation is rate-limiting.

The anomalous decomposition of isopropyl radicals, $CH_3\dot{C}HCH_3 \rightarrow \dot{C}H_3 + CH_2 = CH_2$, is believed[18] to be responsible for the formation of part of the ethylene which is a side product in the pyrolysis of isobutane. The rate constant obtained for this reaction in the temperature range 440 — 541°C and in the pressure range 50 — 150 mmHg agrees to some extent with Heller's results[18] (Table 1). A somewhat different value of the rate constant for this reaction in the temperature range 417 — 493°C was obtained by Kerr and Trotman-Dickenson[20] in the photolysis of isobutyraldehyde.

The β-rule breaks down similarly in the decomposition of butyl radicals. In a study of the photolysis of n-valeraldehyde at 300 — 416°C, the same workers[21] observed a rapid increase of the amount of methane and propene with retention of the ratio [methane]/[propene] ≃ 1. An anomalous decomposition reaction consisting of 1 — 3 migration of hydrogen and the dissociation of the C — C bond,

$$CH_3CH_2CH_2\dot{C}H_2 \rightarrow CH_3\dot{C}HCH_2CH_3 \rightarrow CH_3CH{=}CH_2 + \dot{C}H_3 , \qquad (3)$$

was stated to be the cause of this behaviour.

Table 1. Kinetic parameters of the anomalous decomposition of alkyl radicals.

Reaction	T, °K	$\lg A$ (s^{-1})	E, kcal mole^{-1}	References
$CH_3\dot{C}DCH_3 \rightarrow CH_2CHD + \dot{C}H_3$	686—777	15.05	32.5±2.0	18
iso-$\dot{C}_3H_7 \rightarrow C_2H_4 + \dot{C}H_3$	690—770	10.6	29.5	20
	713—814	12.0±0.2	34.5±0.5	19
	690—814	11.28±0.68	31.88±2.30	25
n-$\dot{C}_4H_9 \rightarrow C_3H_6 + \dot{C}H_3$	523—650	11.0	23	22, 26, 27
	571—689	12.1	27.1	21, 26, 27
n-$\dot{C}_4H_9 \rightarrow$ s-$\dot{C}_4H_9 \rightarrow \dot{C}H_3 + C_3H_6$	913—933	14.71	41.0	23
t-$\dot{C}_4H_9 \rightarrow C_3H_6 + \dot{C}H_3$	742—797	16.0	46.3	24, 27
	—	8.5	18.5	26

As in the work of Heller and Gordon[18], it remained obscure whether the rearrangement occurs before the decomposition or simultaneously with it. The authors believe that isomerisation precedes decomposition: the first reaction stage is exothermic and the s-butyl radical formed has a larger store of energy than is required for decomposition. If such a radical is not deactivated by a collision (the probability of which is small at low pressures), then it will of course decompose.

A reaction similar to reaction (3) was invoked still earlier by Bywater and Steacie[22] to explain the approximate equality of the rates of formation of methane and propene in the photolytic decomposition of n-butane (250 — 400°C, 200 mmHg) sensitised by mercury. A reaction of this kind should be accompanied by 1 — 2 or 1 — 3 migration of hydrogen.

The conclusion that the n-butyl radical isomerises to the s-butyl radical with subsequent decomposition into a methyl radical was also reached by Lin and Back[23] using results on the kinetics of the secondary formation of methane in the thermal decomposition of ethane (550 — 726°C, 10 — 600 mmHg). Probably the reaction does indeed occur in two stages, since for high degrees of conversion the presence of *cis*- and *trans*-but-2-enes in the system may be evidence of the existence of s-butyl radicals.

The isomerisation of t-butyl radicals was studied by Birrell and Trotman-Dickenson[24] in the photoinitiated decomposition of trimethylacetaldehyde. Above 470°C, they obtained considerable amounts of propene and methane. The authors explain this by isomerisation reactions followed by the decomposition of the t-butyl radical:

$$(CH_3)_2\dot{C}CH_3 \rightarrow (CH_3)_2CH\dot{C}H_2 \rightarrow CH_3CH{=}CH_2 + \dot{C}H_3 . \qquad (4)$$

Thus it is evident that a number of studies appear to indicate the possibility of hydrogen shifts via a three-membered cyclic transition state under the usual experimental conditions of cracking and photolysis reactions. Table 1 lists the kinetic parameters of such reactions.

However, there exists no less convincing evidence that the decomposition of hydrocarbon radicals takes place always in accordance with the β-rule. Thus Jackson and McNesby[28] studied the thermal decomposition of [1,1,1-D_3]propane at 472 — 553°C and a pressure of about 50 mmHg. Under these conditions, the n-propyl radical decomposes rapidly into ethylene and a methyl radical, while for the isopropyl radical four possible decomposition pathways were suggested:

$$CD_3\dot{C}HCH_3 \rightarrow [\dot{C}D_2CHDCH_3] \rightarrow CD_2{=}CDH + \dot{C}H_3, \quad (5)$$

$$CD_3\dot{C}HCH_3 \rightarrow [CD_3CH_2\dot{C}H_2] \rightarrow \dot{C}D_3 + C_2H_4, \quad (6)$$

$$CD_3\dot{C}HCH_3 \rightarrow \dot{D} + CD_2{=}CH{-}CH_3, \quad (7)$$

$$CD_3\dot{C}HCH_3 \rightarrow \dot{H} + CD_3{-}CH{=}CH_2. \quad (8)$$

The authors detected 3% of C_2H_3D which they believe to have been formed via reaction (5). The ratio of the yield of ethylene formed as a result of isomerisation to the yield of propene is given by the ratio $(k_5 + k_6)/(k_7 + k_8)$ and corresponds to k_9/k_{10} for the reactions

$$CH_3\dot{C}HCH_3 \rightarrow [CH_3CH_2\dot{C}H_2] \rightarrow \dot{C}H_3 + C_2H_4, \quad (9)$$

$$CH_3\dot{C}HCH_3 \rightarrow \dot{H} + C_3H_6. \quad (10)$$

In the above temperature range, the ratio is on average 0.88. In general, this value increases with temperature, although some investigators[18,29] noted the opposite behaviour. Thus, despite the fact that the above investigation does not involve the rejection, in principle, of the possibility of the $3ps$ isomerisation of a small radical, under the usual cracking conditions this process takes place to only a small extent and can hardly compete with other reactions of the isopropyl radical.

The photolysis of di-isopropylmercury in a flow system at 150 — 300°C and a pressure of about 4 mmHg has been investigated[30]. Only one C_6 hydrocarbon (2,3-dimethylbutane, formed by the recombination if isopropyl radicals) was obtained. There is no isomerisation of iso-$\dot{C}_3H_7$ to n-$\dot{C}_3H_7$. However, the presence in the reaction products of isobutane and ethylene suggests the reaction

$$CH_3\dot{C}HCH_3 \rightarrow \dot{C}H_3 + CH_2{=}CH_2,$$

which is fully in agreement with the data of Heller and Gordon[18]. The results of a study by Billinge and Gowenlock[30] suggest that the decomposition and isomerisation stages take place simultaneously. This is indicated by the absence from the system of other isomeric hexanes following the addition of perfluorocyclohexane. Since even in the presence of the additive the pressure in the system did not exceed about 4.5 mmHg, deactivation due to perfluorocyclohexane is unlikely.

McNesby et al.[31] studied the pyrolysis of acetone in the presence of n-[2,2,3,3-D_4]butane at 365 — 506°C and 32 mmHg. Two decomposition pathways were suggested for each butyl radical:

$$\dot{C}H_2CD_2CD_2CH_3 \rightarrow \left[\begin{array}{c} D \\ \diagup \\ CH_2{-}CDCD_2CH_3 \end{array}\right] \rightarrow CH_2DCD{=}CD_2 + \dot{C}H_3, \quad (11)$$

$$\dot{C}H_2CD_2CD_2CH_3 \rightarrow CH_2{=}CD_2 + CD_2CH_3, \quad (12)$$

$$CH_3\dot{C}DCD_2CH_3 \rightarrow \left[\begin{array}{c} CH_2{-}CDCD_2CH_3 \\ \diagdown \\ H \end{array}\right] \rightarrow CH_2{=}CDH + CD_2CH_3, \quad (13)$$

$$CH_3\dot{C}DCD_2CH_3 \rightarrow CH_3CD{=}CD_2 + \dot{C}H_3. \quad (14)$$

The study of the mass spectra of the ethylene (mainly $CH_2 = CD_2$) and propene fractions led to the conclusion that reactions (12) and (14) predominate. Reaction (11), the 1 — 2 migration of deuterium, is not particularly important, since the amount of [D_4]-propene is not more than 1% of the main product—[D_3]propene. [D]ethylene is formed to a very slight extent or not at all. Thus isomerisations of the $3sp$ and $3ps$ types occur to an insignificant extent under the above experimental conditions.

Nevertheless the formation of [D_3]propene as the main product does not always imply a low degree of isomerisation of the butyl radical[21,24]. The formation of such propene can be accounted for also by the 1 — 3 migration of deuterium followed by decomposition via a reaction analogous to reaction (3):

$$\dot{C}H_2CD_2CD_2CH_3 \rightarrow CH_2DCD_2\dot{C}DCH_3 \rightarrow CH_3CD{=}CD_2 + \dot{C}H_2D.$$

In their study of the isotope composition of the methane fraction, Gordon and McNesby[32] did not detect dideuteriomethane, which should have been formed since under these conditions (400 — 450°) methyl radicals abstract deuterium more than twice as readily as hydrogen. However, the yields of methane and propene in the study by Kerr and Trotman-Dickenson[21] can be accounted for by the abstraction by free radicals of equivalent hydrogen atoms from n-valeraldehyde at the β- and γ-carbon atoms with subsequent decomposition of the large radicals:

$$\dot{R} + CH_3CH_2CH_2CH_2CHO \rightarrow RH + CH_3\dot{C}HCH_2CH_2CHO \rightarrow CH_3CHCH_2 + \dot{C}H_2CHO,$$
$$\dot{R} + CH_3CH_2CH_2CH_2CHO \rightarrow RH + CH_3CH_2\dot{C}HCH_2CHO \rightarrow \dot{C}H_3 + CH_2CHCH_2CHO.$$

Frey and Hepp[33], who studied the decomposition of di-n- and di-s-butylmercury at 490°C and 1 — 5 mmHg, also found that the decomposition of the n- and s-butyl radicals takes place in accordance with the β-rule and the isomerisation n-$\dot{C}_4H_9 \rightleftharpoons$ s-$\dot{C}_4H_9$ with subsequent decomposition takes place to only a very slight extent (about 0.1%) under these conditions if at all. It was also shown[34] that, at low pressures and at 350 — 525°C, the n-butyl radical decomposes only into ethylene and an ethyl radical and the s-butyl radical decomposes only into propene and a methyl radical. The decompositions of n-butyl and t-isobutyl radicals take place in accordance with the β-rule.

The isomerisations of isobutyl radicals were also studied by McNesby and Jackson in the thermal decomposition of [2-D]isobutane at 45 — 56 mmHg.[35] At 540°C the rate of the isomerisation reaction

$$(CH_3)_2\,CD\dot{C}H_2 \rightarrow (CH_3)_2\,\dot{C}CH_2D$$

is only one hundredth of the rate of the direct decomposition

$$(CH_3)_2\,CD\dot{C}H_2 \rightarrow \dot{C}H_3 + CH_3CD{=}CH_2.$$

Thus the results quoted show that the usual experimental technique and method do not allow a solution of the problem of the possible 1 — 2 or 1 — 3 migration of hydrogen in alkyl radicals and indicate only an unimportant role of these processes in the cracking and photolysis of many organic compounds. In particular, the β-rule holds with a high degree of precision for the decomposition of alkyl radicals.

The $3sp$ isomerisation of n-$\dot{C}_3H_7$ and iso-$\dot{C}_3H_7$ is also insignificant. In the study already discussed[30], the only hexane obtained in the photolysis of di-n-propylmercury at 380 — 460°C was n-hexane. Similarly in the photolysis of di-n-propyl ketone (55 — 357°C, 8 — 115 mmHg), 98% of the C_6 fraction consisted of n-hexane[36]. Lossing and de Sousa[34] also showed that the decomposition products of n-propyl radicals are ethylene and methyl radicals.

The most accurate results, whereby it is possible to infer the occurrence of 1 — 2 migration of hydrogen in radicals in both gaseous and liquid phases, were obtained in a tracer atom study employing hydrogen and carbon isotopes. Brown and Russell[37] chlorinated photochemically 2-methyl-[2-D]propane at −15°C. The products were t-butyl chloride, isobutyl chloride, hydrogen chloride, and deuterium hydride. This indicates the occurrence of two reactions:

$$(CH_3)_2CDCH_3 + Cl_2 \rightarrow (CH_3)_2CD\dot{C}H_2 + HCl, \quad (A)$$

$$(CH_3)_2CDCH_3 + Cl_2 \rightarrow (CH_3)_2\dot{C}CH_3 + DCl. \quad (B)$$

The occurrence of the rearrangement of radicals (A) and (B) was inferred from the DCl/HCl and t-butyl chloride/isobutyl chloride ratios respectively. The excellent agreement between these ratios clearly indicates the absence of any considerable degree of isomerisation with transfer of hydrogen according to the mechanisms

$$(CH_3)_2CD\dot{C}H_2 \rightarrow (CH_3)_2\dot{C}CH_2D \text{ and } (CH_3)_2\dot{C}CH_3 \rightarrow (CH_3)_2CH\dot{C}H_2,$$

$$(CH_3)_2CDCH_2 + (CH_3)_2CDCH_3 \rightarrow (CH_3)_2CDCH_2D + (CH_3)_2\dot{C}CH_3,$$

which constitutes essentially intermolecular isomerisation.

On the other hand, Bhardwaj and Lee[38] studied the isomerisation of [1-^{14}C]ethyl iodide and [2-^{14}C]ethyl iodide under the influence of γ-radiation and observed that at room temperature in a 2% aqueous solution of [1-^{14}C]ethyl iodide 0.28 of a molecule of [2-^{14}C]ethyl iodide is formed for each 100 eV of absorbed energy regardless of radiation dose†. However, the addition of 1% of iodine before irradiation lowers the degree of rearrangement to zero. The authors believe that the most probable process mechanism involves 1 — 2 migration of hydrogen:

$$CH_3-{}^{14}\dot{C}H_2 \rightarrow \dot{C}H_2{}^{14}CH_3. \quad (15)$$

The effect of iodine can be explained by a higher rate of its addition to the ethyl radical compared with reaction (15). The formation of [2-^{14}C]ethyl iodide via a different pathway, namely by the reaction between the main products (ethylene and hydrogen iodide),

$$CH_2={}^{14}CH_2 + HI \rightarrow CH_2I-{}^{14}CH_3,$$

is possible in principle but the marked inhibiting effect of iodine would then be unexplained. Similarly, when a 2% aqueous solution of [1-^{14}C]ethanol is irradiated with γ-rays, [2-^{14}C]ethanol with $G \simeq 0.04$ is formed[39], which is also evidence of a hydrogen shift. The higher value of G found by Bhardwaj and Lee[38] can be accounted for by the greater ease of formation of the ethyl radical from ethyl iodide than from ethanol.

There are also many experimental data of a different type, indicating the possibility of the migration of a hydrogen atom to an adjoining carbon atom with a free valence. Thus Callear and Cvetanović[40], who studied the mercury-photosensitised decomposition of C_2H_4, C_2D_4, and *cis*-$C_2D_2H_2$ at room temperature and 16 — 750 mmHg, found that the main products in this process (hydrogen and acetylene) are not obtained by a radical mechanism but in consequence of homogeneous intermolecular processes. In the photolysis of *cis*-$C_2D_2H_2$, the isotopic composition of the hydrogen formed corresponds to the ratios $H_2 : HD : D_2 = 2 : 5.7 : 1$. One explanation of this finding involves the recognition that hydrogen may migrate in excited species. The available data do not allow a rigorous proof of the process mechanism but the migration of hydrogen between carbon atoms is supported by the isomerisation of *cis*-$C_2H_2D_2$ to the *anti*-form, which can occur even on impact deactivation of the excited species (in the presence of a large amount of added carbon dioxide). On the other hand, if in the excited state of ethylene the hydrogen atoms exchange with one another, the hydrogen isotope composition should be identical regardless of whether *cis*- or *anti*-$C_2H_2D_2$ undergoes the mercury-sensitised decomposition. In the decomposition of *anti*-$C_2H_2D_2$, the hydrogen isotope composition corresponds to the ratios $H_2 : HD : D_2 = 1.8 : 4.6 : 1$.[41] This shows that intramolecular hydrogen exchange occurs in ethylene excited with $Hg(^3P_1)$. However, Okabe and McNesby[42] believe that this process is unlikely in direct photolysis *in vacuo* by ultraviolet radiation (1849 — 1236 Å).

Scala and Ausloos[43], who investigated the photolysis of $(CH_3)_2CDCH_2CH_3$ and $(CH_3)_2CHCH_2CH_3$ with light at a wavelength of 1048 — 1470 Å at a pressure of several mmHg, concluded that the rearrangements $CH_3\ddot{C}CH_3 \rightarrow CH_3CH = CH_2$ and $\ddot{C}HCD_3 \rightarrow CHD = CD_3$ take place in the propylidene and ethylidene biradicals respectively. Similarly studies of the photolysis of ethane (1048 — 1067 Å) showed[44-52] that for the above energies the most important process is splitting off of molecular hydrogen, which involves almost exclusively only one carbon atom. The vibrationally excited ethylidene formed on deactivation rearranges to ethylene: $\ddot{C}HCH_3^* \xrightarrow{M} CH_2 = CH_2$. Similar rearrangements with 1,2-shifts of hydrogen or deuterium were observed in the photolysis of other compounds. The 3*sp* migration of hydrogen in the trimethylene biradical occurs in the isomerisation of cyclopropane to propene (see the review by Lazár and Kysel[9]). It was found that[53] the activation energy for the transition

$$\dot{C}H_2CH_2\dot{C}H_2 \rightarrow CH_2{=}CHCH_3$$

is only 9.5 kcal mole^{-1}.

There are many experimental data indicating the occurrence of rearrangements of hydrocarbon radicals also in the solid phase. Ayscough et al.[54] observed a change in the hyperfine structure of the ESR spectrum of the n-propyl radical, reflecting the transformation of the latter into an isopropyl radical, and a spontaneous transformation of the spectrum of the isobutyl radical into that of the t-butyl radical. These transitions occur at the temperature of liquid nitrogen. A similar situation was observed by Iwasaki and Toryama[55] in an ESR study of the photoinduced radical transformation of isobutyl bromide at 77°K. γ-Irradiation of this compound leads to the formation of primary isobutyl radicals which during the period of storage (about 40 days) in the dark at 77°K are spontaneously converted into t-butyl radicals. Illumination of the latter with ultraviolet light at the same temperature for 90 min yields isobutyl radicals, i.e.

$$CH_3-\underset{|}{\overset{CH_2Br}{CH}}-CH_3 \xrightarrow[77°K]{\gamma} CH_3-\underset{|}{\overset{\dot{C}H_2}{CH}}-CH_3 \underset{h\nu}{\rightleftarrows} CH_3-\underset{\cdot}{\overset{CH_3}{C}}-CH_3.$$

Similar transitions occur on γ-irradiation of many polymers at 77°K. The process involving polypropylene[56] takes place as follows:

$$\text{polypropylene} \xrightarrow[77°K]{\gamma} \ldots CH_2-\underset{|}{\overset{\dot{C}H_2}{CH}}-CH_2 \ldots \underset{h\nu}{\rightleftarrows} \ldots CH_2-\underset{\cdot}{\overset{CH_3}{C}}-CH_2.$$

In general one may say that, under the influence of ultraviolet light, 3*pt* migration of hydrogen takes place at the temperature of liquid nitrogen with formation of an

† The number of molecules undergoing rearrangement following the absorption of 100 eV of energy is designated by the symbol G.

energetically more favourable radical. As was to be expected, the reverse process occurs spontaneously.

The isomerisation of radicals in the gas phase with 1 — 2 migration of hydrogen has not yet been investigated even qualitatively. The data examined suggest that the process can occur in principle. It is undoubtedly difficult under the usual conditions in the cracking of hydrocarbons (up to 600°C) but probably occurs in reactions of "hot" species and also in free-radical processes where subsequent reactions of the radical are "slow". Possibly intramolecular rearrangements of the simplest alkyl radicals might be observed in the study of processes at higher temperatures (about 1000 — 1500°C) and lower pressures.

III. 1 — 3 MIGRATION OF A HYDROGEN ATOM

Even fewer data have been obtained for the 4*ab* migration of hydrogen atoms in alkyl radicals in the gas phase. Apart from the studies by Trotman-Dickenson already mentioned[21,24], one may point to the work of Rabinovitch and coworkers[14], who studied the intramolecular isomerisation of many vibrationally excited alkyl radicals and concluded that rearrangements with $N < 5$ are insignificant and cannot occur as simple hydrogen transfers.

The possibility of 1 — 3 migration of hydrogen is indicated by a study of Reutov and Shatkina[57]. Using the carbon-14 isotope, they found that the free propyl radical formed on thermal decomposition in boiling carbon tetrachloride of n-butyryl peroxide labelled in the α-position,

$$(CH_3CH_2{}^{14}CH_2COO)_2 \rightarrow 2CH_3CH_2{}^{14}\dot{C}H_2 + 2\,CO_2,$$

isomerises with migration of a hydrogen atom from the β-position:

$$CH_2CH_2{}^{14}\dot{C}H_2 \rightleftarrows \dot{C}H_2CH_2{}^{14}CH_3. \qquad (16)$$

Analysis of the decomposition products showed that under these conditions such isomerisation occurs to the extent of 4.0 ± 0.5%. In their attempt to confirm reaction (16) by an independent method, Reutov et al.[58] studied the pyrolysis of [α-D_2]butyryl peroxide in boiling carbon tetrachloride. Together with the normal product, the formation (in an amount of 1.3 ± 0.1%) of the anomalous product $CD_2HCH_2CH_2Cl$ was observed, which also indicates the occurrence of the isomerisation reaction (16). The replacement of carbon tetrachloride by bromoform as a solvent leads to a decreased yield of the rearranged product (0.68 ± 0.1% at 140°C),[59] which can be explained by a decrease of the lifetime of the free radical. It was also shown that the structure of the rearrangement product cannot be accounted for by exchange reactions during analysis. One piece of evidence for the possibility of 1 — 3 migration of hydrogen, which is interesting rather than convincing, is provided by the experiments of Voevodskii and coworkers[60-63]. The authors showed by kinetic calculations[60] that the higher rate of exchange of hydrogen for deuterium in alkyl radicals observed in various studies at room temperature can be explained by the reactions $RH + D_2 \rightarrow RD + HD$, $RHD + D_2 \rightarrow RD_2 + HD$, etc., with only the hydrogen atoms linked to the carbon atom with a free valence being capable of undergoing exchange. However, further studies[61-63] showed that this limitation extends only to adjacent carbon atoms. If a free valence can migrate spontaneously to another carbon atom, further hydrogen exchange is probable. As a result, a radical with a higher deuterium content should be formed than in the absence of isomerisation. It has been shown for isobutyl radicals formed by the reaction $(CH_3)_2C = CH_2 + D \rightarrow (CH_3)_2C\dot{C}H_2$ that the fraction of C_8 hydrocarbons, which are formed by the recombination of these radicals, is characterised by a degree of exchange of 40 — 50%, while without allowance for isomerisation the maximum degree of exchange should be 30%.[61] Consequently the following isomerisations are possible at room temperature:

$$CH_3(CH_3)\,C\dot{C}H_2 \rightleftarrows CH_3(\dot{C}H_2)\,CCH_3 \rightleftarrows \dot{C}H_2(CH_3)\,CCH_3$$

in which 1 — 3 migration of hydrogen takes place. On the other hand, it has been shown for the isopropyl radical and radicals of the type $(CH_3)_2C\dot{C}(CH_3)_2$ that the migration of the free valence to an adjacent carbon atom is impossible[63].

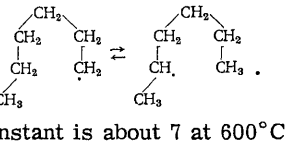
A weak feature of these experiments is the experimental technique. Atomic hydrogen was withdrawn from the discharge tube and was directed to the reactor mixed with the hydrocarbon and deuterium under a pressure of 0.2 — 0.4 mmHg at a rate up to 3 m s^{-1}. Although separate experiments showed that under these conditions the hydrocarbon hardly reached the discharge zone (the concentration of RH in the discharge zone was ≤0.25%[63]), the rate of diffusion of deuterium may be higher and the investigators might have dealt with atomic and not molecular deuterium. In this case the high degree of deuteriation cannot be accounted for by radical rearrangements.

Chesick[64], who investigated the photolysis of *cis*-but-2-ene by light at a wavelength of 2026 — 2062 Å at room temperature and 540 mmHg, concluded that 1 — 3 migration of hydrogen in the unsaturated radical $CH_3CH = \dot{C}H$ does occur:

$$CH_3CH{=}\dot{C}H \rightarrow \dot{C}H_2CH{=}CH_2.$$

IV. MIGRATION OF A HYDROGEN ATOM TO A MORE REMOTE CARBON ATOM WITH A FREE VALENCE

Rearrangements of this kind were first suggested in 1943 by Kossiakoff and Rice[65]. They believe that alkyl radicals containing five or more carbon atoms can isomerise under the usual cracking conditions. The activation energy for such isomerisation may be much lower than the decomposition energy of the radical. As a result, equilibrium should be established between two isomeric forms, for example in the isomerisation of primary n-hexyl radicals:



The equilibrium constant is about 7 at 600°C. The authors employed this hypothesis to calculate the thermal decomposition products of n-hexane and certain octanes. It was found that the calculation which includes the possibility of an intramolecular hydrogen transfer agrees better with experiment than calculation which neglects isomerisation. For radicals with longer chains, for example as obtained in the cracking of n-hexadecane[66], there is an even greater number of possibilities of isomerisation and the improvement of the agreement between the yield of reaction products and the calculation becomes even more marked when these possibilities are taken into account. Somewhat later Sefton and LeRoy[67] studied at 250 — 300°C the polymerisation of ethylene initiated by ethyl radicals labelled with carbon-14 in the methyl group.

2-Methylbut-1-ene was detected in the reaction products. If this product were formed by the addition of a labelled ethyl radical to propene with subsequent disproportionation of the 2-methylbutyl radical, its molar radioactivity should have been unity. Experiment however, yielded a value equal to only half that quantity. The authors explain the discrepancy by intramolecular radical isomerisation involving 1 — 4 and 1 — 5 migration of hydrogen.

No less convincing are the quantitative results of the experiments by Gordon and McNesby[68], who also investigated the reaction of methyl radicals with ethylene in the temperature range 300 — 500°C and at pressures in the range 109 — 360 mmHg. Under these conditions, the main product is propene. The authors suggest the following process mechanism:

$$\dot{C}H_3 + CH_2{=}CH_2 \rightarrow CH_3CH_2\dot{C}H_2 \xrightarrow{+CH_2=CH_2} CH_3CH_2CH_2CH_2\dot{C}H_2,$$

$$CH_3CH_2CH_2CH_2\dot{C}H_2 \rightarrow CH_3\dot{C}HCH_2CH_2CH_3 \rightarrow CH_3CH{=}CH_2 + \dot{C}_2H_5.$$

The reaction mixture contains also but-1-ene obtained as a result of a 1,5-rearrangement of heptyl radicals:

$$CH_3(CH_2)_3\dot{C}H_2 + CH_2{=}CH_2 \rightarrow CH_3(CH_2)_5\dot{C}H_2 \rightarrow CH_3CH_2\dot{C}H(CH_2)_3CH_3 \rightarrow$$
$$\rightarrow CH_3CH_2CH{=}CH_2 + \dot{C}H_2CH_2CH_3.$$

The validity of the above mechanism was demonstrated by the introduction of CD_3 radicals. At 300°C the propene fraction had the following isotope composition: 30% C_3H_6, 20% C_3H_5D, 30% $C_3H_4D_2$, and 20% $C_3H_3D_3$. This indicated the occurrence of exchange processes. One of the possible mechanisms, involving a number of rapid hydrogen exchanges between carbon atoms in the 1- and 4-positions and in the 1- and 5-positions, can be represented as follows:

$$CD_3(CH_2)_3\dot{C}H_2 \xrightarrow{1,5} \dot{C}D_2(CH_2)_3CH_2D \xrightarrow{1,5} CD_2H(CH_2)_3\dot{C}HD \rightarrow \text{etc.},$$
$$\downarrow 1,4 \qquad\qquad \downarrow 1,4 \qquad\qquad \downarrow 1,4$$
$$CD_3\dot{C}H(CH_2)_2CH_3 \rightarrow CD_3CH{=}CH_2 + \dot{C}_2H_5 \mid CD_2H\dot{C}H(CH_2)_2CH_2D \rightarrow CD_2HCH{=}CH_2 + \dot{C}_2H_4D,$$
$$\downarrow$$
$$CD_2H(CH_2)_2\dot{C}HCH_2D \rightarrow \dot{C}_2H_3D_2 = CH_2{=}CHCDH_2.$$

Wijnen[69], who photolysed heptan-2-one at 60 — 200°C, detected 2-methylpentane among the reaction products. This compound is produced by combinations of methyl and s-pentyl radicals. Consequently the reaction $\dot{C}H_2(CH_2)_3CH_3 \rightarrow CH_3(CH_2)_2\dot{C}HCH_3$ with 1 — 4 hydrogen migration plays a significant role not only at 250°C as, in the work of Gordon and McNesby[68], but also at a temperature as low as 150°C.

There are reliable data indicating the migration of hydrogen atoms in radicals in the liquid phase. For example, in a study of the telomerisation of ethylene by acetic acid at 140°C, Freidlina et al.[70] detected isoacids (α-ethylcaproic and α-n-butylcaproic acids) in the products. The formation of these acids can be readily explained by a rearrangement of $\dot{C}H_2CH_2CH_2CH_2CH_2COOH$ to $CH_3CH_2CH_2CH_2\dot{C}HCOOH$. On the other hand, the absence of isohexanoic acid from the reaction mixture indicates the impossibility of 1 — 3 migration of hydrogen in the $\dot{C}H_2CH_2CH_2COOH$ radical under these conditions. It has also been shown[71] that, as was to be expected, an increase of temperature favours the formation of a rearranged product, while a change in the concentration of the reactants does not have a significant influence on the yield.

Rearrangements similar to that indicated above occur also in the telomerisation of ethylene by methyl chloroacetate[72], methyl alcohol[72], propionic acid[73], methyl propionate[73], acetoacetic ester[73], etc. Probably, if the temperatures are sufficiently high and the telogens are comparatively ineffective, the rearrangement of radicals with 1 — 5 migration of hydrogen is a general phenomenon[72].

However, whereas radical isomerisation plays an appreciable role in solutions of relatively inactive telogens, in the telomerisation of ethylene in carbon tetrachloride solutions (at 140°C)[74-76] its importance is low. On passing to the gas phase (at a pressure of about 0.3 atm), 70 — 80% of the products are isomers of the normal telomers. Under these conditions, unimolecular rearrangements compete successfully with bimolecular reactions, for example:

$$Cl_3C(CH_2)_5CH_2- \begin{cases} \xrightarrow{+CCl_4} Cl_3C(CH_2)_5CH_2Cl & (38\%), \\ \xrightarrow{+C_2H_4} Cl_3C(CH_2)_7\dot{C}H_2 & (\sim 4\%), \\ \xrightarrow[\text{rearrangement}]{} Cl_3CCH_2\dot{C}H(CH_2)_3CH_3 & (\sim 58\%) \text{ etc.} \end{cases}$$

The contribution of such rearrangements diminishes very markedly with increase of pressure and ethylene and carbon tetrachloride concentrations.

Intramolecular rearrangements of radicals in the solid phase have also been mentioned[77,78]. A study of the hyperfine structure of the ESR spectra of alkyl radicals formed from n-hexadec-1-ene, n-dec-1-ene, n-oct-2-ene, n-hept-2-ene, etc. on irradiation with γ-rays (at 77°K) showed that they are spontaneously converted into energetically more favourable allylic radicals:

$$CH_2-\dot{C}H-(CH_2)_n-CH{=}CH-CH_2 \underset{h\nu}{\rightleftarrows} CH_2-(CH_2)_n-\dot{C}H-CH{=}CH-CH_2.$$

Under these conditions, the overall spin concentration remains constant. The reverse transition at liquid nitrogen temperature can be achieved on irradiation with ultraviolet light ($\lambda \leqslant 3400$ Å).

During recent years, the first quantitative data have been obtained for type 5*sp* and 6*sp* isomerisation rate constants. In a study of the photolysis of a mixture of acetone and ethylene (165 — 230°C, $P \simeq 104$ mmHg), Endrenyi and LeRoy[79] succeeded in estimating quantitatively the relative contributions of the reactions of n-propyl radicals. The radicals were obtained by the addition of $CH_3^{\cdot}$ to ethylene. The presence of isohexane among the reaction products was regarded by the authors as evidence that some of the n-pentyl radicals isomerise to s-pentyl radicals. The rate constant for the rearrangement

$$\text{n-}\dot{C}_5H_{11} \rightarrow \text{s-}\dot{C}_5H_{11} \qquad (17)$$

was found to be

$$k_{17} = 10^{7.146} \exp(-10800/RT)\ s^{-1}.$$

Watkins and Ostreko[80] studied the photolysis of a mixture of azobutane and ethylene at temperatures in the range 79 — 132°C and a pressure of about 55 mmHg. The presence of s-hexyl radicals in the system is indicated by the presence of 3-methylheptane in the products. Using the method of a previous investigation[79], the rate constant for the isomerisation

$$\text{n-}\dot{C}_6H_{13} \rightarrow \text{s-}\dot{C}_6H_{13}, \qquad (18)$$

was determined:

$$k_{18} = 10^{7.3 \pm 1.0} \exp[(-8300 \pm 1700/RT)]\ s^{-1}.$$

Rabinovitch and coworkers[14] studied the isomerisation of vibrationally excited alkyl radicals: heptyl-3· (Hp3·), octyl-4· (Oc4·), octyl-2· (Oc2·), 3-methylpentyl-2· (3MP2·), nonyl-2· (N2·), 3-methylhexyl-2· (3MH2·), and 3,3-dimethylhexyl-2· (33DMH2·). In all cases the radicals formed were chemically activated by the addition of a hydrogen atom to the corresponding alkene at room temperature. The results are compiled in Table 2, which also includes the rate constants for the competing isomerisation reactions expressed relative to the 5*ss* process, the rate of which was assumed to be unity.

Table 2 shows that the radicals the isomerisation of which is energetically feasible (i.e. for $N \geqslant 5$) rearrange almost completely and in most cases the isomerisation is the fastest process among those occurring in the given systems.

Table 2. Relative rates of isomerisation of radicals.

Radical	5sp	5 ss	5 pp	6 sp	6 ps	6 ss	7 ss	Products and absolute rates of dissociation of C-C bonds, 10^5 s^{-1}	
Hp3·	—	1(7.5)[a]	—	—	<1(<7.5)	—	—	B1+*n*-Pr·	1.2
Oc4·	—	1(2.1)	—	—	—	—	—	H1+Et	0.14
Oc2·	—	1(8)	—	—	—	75(600)	—	Pr1+P1·	1.0
N2[b]	—	1(20)	—	—	—	100(2000)	5(100)	Pr1+H1·	0.09
Oct[b]	—	—	(<0.05)	(>300)	—	—	—	C_2H_4+H1·	1.0
3HP1[b]	(<0,5)	—	—	—	—	—	—	C_2H_4+SBu·	20.0
3MH2·	—	(2.5)	—	—	—	—	—	t- B2+n- Pr·	4.0
3MH1·	—	—	—	(>100)	—	—	—	C_2H_4+P2·	10.0
33DMH2·	—	(7.0)	—	—	—	—	—	2MB$_2$+n-Pr	2.3
33DMH1·	—	—		(<200)	—	—	—	C_2H_4+2MP2·	4.0

[a] The numbers in round brackets denote the ratio of the rate of isomerisation to the rate of decomposition indicated in the last column.

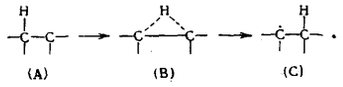
[b] The rates of decomposition have been estimated to within a factor or two.

Examination of the data leads to the conclusion that the isomerisation of alkyl radicals with hydrogen migration, proceeding via five-, six-, and seven-membered cyclic transition states, is possible. This process must undoubtedly be taken into account when specific free-radical reactions are considered.

V. THE MECHANISM OF THE MIGRATION OF HYDROGEN IN ALKYL RADICALS

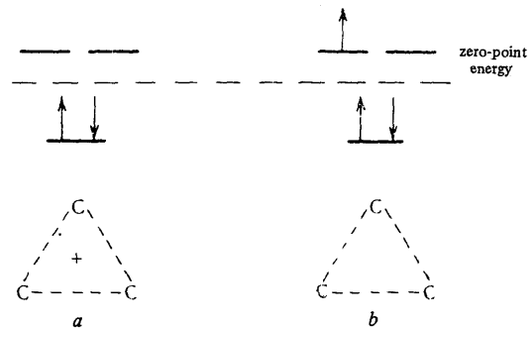
When examining the literature on the rearrangement of alkyl radicals, one cannot avoid the problem of the mechanism of hydrogen migration. Unfortunately the detailed mechanisms of the rearrangements have been little investigated and only hypothetical views have been expressed on this problem.

At the present time the hypothesis of Kossiakoff and Rice[65] that hydrogen migration in long-chain radicals proceed via a cyclic transition state is generally accepted. However, the possibility of forming a three-membered complex on transfer of hydrogen from a carbon atom to an adjacent carbon atom is nevertheless still open to some doubt[14]. Indeed approximate quantum-mechanical calculations show that a three-membered transition state should have a high activation energy, since "attack" on the bond takes place at an angle different from the most favourable angle, as a result of which the ring is strained[10,11]. In the rearrangement of a substance (A) to a substance (C), there is an intermediate with a configuration (B):



(A) (B) (C)

The activation energy for the rearrangement is determined by the energy difference between the compound (A) and the intermediate complex (B). The triatomic structure (B) has three orbitals, one of which is bonding and the other two are degenerate antibonding. In the case of the carbonium ion, the tendency of which to rearrange is well known, there are only two electrons and these can be assigned to the lowest bonding orbital (Fig. *a*).



Energy levels for a three-orbital three-carbon system[11].

The free electron of the radical must pass to one of the antibonding orbitals (Fig. *b*) which destabilises the system and increases its energy. The stabilisation and decrease of the energy of the transition state (B) are achieved by a redistribution of electron density which occurs during the shift of the migrating group, which in turn is determined by its nature (see for example data on the migration of aryl groups[81]). On the other hand, the 1 — 2 migration of halogen atoms, which take place fairly readily[13], cannot be understood on the basis of the foregoing considerations. Mayants[82] explains this contradiction by a difference between the vibration frequencies and modes of substituted and unsubstituted radicals. He believes that the rate of rearrangement is largely determined by the probability of the occurrence of the required transitional configuration as a result of intramolecular vibrations. On the other hand, the probability of the formation of such a transition state increases, other conditions being equal, with decrease of the vibration frequencies. One may expect[72] that, for radicals containing a halogen atom or an aryl group in the α-position relative to the free valence, the frequencies of the vibrations responsible for the formation of the transitional configuration will decrease in relation to unsubstituted radicals both as a result of the increase of the mass of the substituent and probably owing to a decrease of the deformation force constant. Therefore in substituted radicals one should expect an increase of the rearrangement rate constant (the 1 — 2 migration of the halogen and the aryl group) compared with the rearrangement of the unsubstituted radical (1 — 2 migration of hydrogen). If, on the other hand, the substituent is an alkyl group, then, according to Freidlina[72], isomerisation involving the migration of hydrogen atoms more remote from the radical centre and a more favourable angle of attack may compete with the 1 — 2 migration of the alkyl group.

On the other hand, if 1 — 2 and 1 — 3 migration of hydrogen is difficult on energetic grounds, the steric factors governing the rate constants for such processes should be fairly high. Indeed, within the framework of

absolute reaction rates, the pre-exponential factor for gas-phase reactions

$$A = \varkappa e \frac{kT}{h} e^{\frac{\Delta S^+}{R}}$$

is determined by the activation entropy ΔS^*, which is equal to the difference between the entropies of the activated and initial states of the system. For reactions proceeding via a three-membered cyclic activated complex, the entropies of the complex and the reactant differ mainly in terms corresponding to the loss of one hindered internal rotation and the change of the frequencies in the activated complex. This difference is of the order of −4 cal mole^{-1} deg^{-1}. On the other hand, rearrangements proceeding via five- and six-membered, etc. transition states lead to a loss of 4, 5, and more internal rotations in the complex. This greatly reduces the A factors for such rearrangements. Thus we observe the following situation: processes with 1 — 2 migration of hydrogen are characterised by a high activation energy and a high pre-exponential factor, while the kinetic parameters for many-centre processes are lower. Therefore in the series of 1 — 2, 1 — 3, 1 — 6, ... migrations of hydrogen one should expect the appearance of a compensation effect.

It is noteworthy that the anomalously low pre-exponential factors for reactions (17) and (18) cannot be accounted for within the framework of the theory of absolute reaction rates. This led Endrenyi and LeRoy to the conclusion[79] that reaction (17) has a transmission coefficient $\varkappa \ll 1$. However, experiments with added inert gases[80] did not show changes in the measured rate constant, which is evidence that the process is adiabatic. In order to account for the extremely low entropy of activation for these reactions, Watkins and Ostreko[80] proposed the model of a "rigid" cyclic transition state with very strong terminal interactions due to the fact that the hydrogen atom belongs to both "ends" of the radical. In this case the force constants of the low-frequency vibrations in the complex increase rapidly, which causes a decrease in entropy activation for the reaction in addition to a decrease owing to the loss of capacity for certain types of internal rotation.

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