

Isomerization of Vibrationally Excited Alkyl Radicals by Hydrogen Atom Migration^{1a}

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Abstract: The intramolecular isomerization (by H atom transfer) of ten different vibrationally excited alkyl radicals was investigated. An H + olefin chemical activation technique was used to produce the excited alkyl radicals in a relatively narrow distribution of energy states centered near 45 kcal mol⁻¹. It was found that reactions which proceed *via* a six-membered ring transition state are most labile; a table of relative isomerization tendency as a function of ring size and H type is given. Isomerization involving four-membered-ring transition states was not observed. The effect of the isomerization process upon our earlier work on alkyl radical decomposition, which failed to recognize it, is considered; improved agreement between theoretical and experimental decomposition rates is obtained. The unusually low preexponential factors previously reported by other workers is discussed.

Alkyl radical isomerization by H atom transfer reactions were first reported some years ago by Kossiakoff and Rice,² who proposed that the activation energy for isomerization of a long-chain free radical may be much less than the activation energy for its decomposition, and who also suggested a cyclic transition state. This was later supported by Gordon and McNesby,³ who found thermal rearrangement of *n*-pentyl (Pl·) and *n*-hexyl (Hl·) radicals at 572–775°K, but not of *n*-butyl. Further evidence of 1–4 and 1–5 intramolecular H migration was obtained by Sefton and LeRoy⁴ in work on ethylene polymerization. Endrenyi and LeRoy⁵ studied the thermal isomerization of Pl· (produced by methyl addition to ethylene followed by further ethylene addition) to pentyl-2 (P2·); they reported a rate constant of $1.4 \times 10^7 \exp(-10.8 \times 10^3/RT)$.

Until recently, all such studies in the gas phase have been made on H-transfer reactions which are thermodynamically favored by about 4 kcal., *i.e.*, the isomerization of primary radicals to form secondary radicals. Studies of competitive unimolecular decomposition reactions of alkyl radicals have recently revealed numerous instances of the rearrangement of secondary radicals.⁶ The present paper presents the results of explicit studies of the isomerization of vibrationally excited heptyl-3· (Hp3·), octyl-4· (Oc4·), octyl-2· (Oc2·), 3-methylpentyl-2· (3MP2·), and nonyl-2· (N2·). The competitive isomerization and consecutive decomposition of excited 3-methylhexyl-2· (3MH2·) and 3,3-dimethylhexyl-2· (33DMH2·) were also studied. In all cases the radicals were chemically activated by H atom addition to the appropriate alkene. H atoms were generated either by Hg photosensitization or by a Wood–Bonhoeffer discharge tube. Both of these methods give rise to radicals which have ~45 kcal of vibrational energy.

(1) (a) This work was supported by the U. S. Office of Naval Research; abstracted in part from the Ph.D. dissertation of C. W. Larson, University of Washington, 1969; (b) NSF predoctoral fellow.

(2) A. Kossiakoff and F. O. Rice, *J. Amer. Chem. Soc.*, **65**, 590 (1943).

(3) A. S. Gordon and J. R. McNesby, *J. Chem. Phys.*, **31**, 853 (1959).

(4) V. B. Sefton and D. J. LeRoy, *Can. J. Chem.*, **34**, 41 (1956).

(5) L. Endrenyi and D. J. LeRoy, *J. Phys. Chem.*, **70**, 4081 (1966).

(6) C. W. Larson, D. C. Tardy, and B. S. Rabinovitch, *J. Chem. Phys.*, **49**, 299 (1968).

Experimental Section

Materials. Hydrocarbons from the following sources were used: Phillips Petroleum research grade butene-1 (B1) and ethylene; Columbia Chemical 3-methylpentene-1 (3MP1); Farchan *trans*-hexene-3 (*t*H3); American Petroleum Institute *trans*-octene-4 (*t*Oc4), octene-1 (Oc1), and 3-methylhexene-1 (3MH1); Chemical Samples 3,3-dimethylhexene-1 (33DMH1) and nonene-1 (N1). When interfering impurities were present, samples were purified by gas chromatography with use of a 12-ft squalane column at temperatures between 70 and 100°. Commercial tank hydrogen was purified by passage through silica gel at –196°.

Apparatus and Procedure. A conventional Pyrex vacuum system fitted with Viton O-ring valves was used. The reactors were 20- and 200-l. flasks fitted with quartz lamp wells. A GE 8-W germicidal lamp was used for the mercury photosensitization of hydrogen. A Wood–Bonhoeffer discharge tube could be mounted so that an exit slit (capillary) was in the center of a 70-l. Pyrex flask. Pressures were measured with a calibrated McLeod gauge or with a conventional manometer.

A standard mixture of hydrogen–alkene was made and stored. Aliquots were taken and expanded into the reactor; reaction times were between 10 and 70 min; the percentage reaction was of the order of 10%. The reactant and products were pumped through glass wool packed traps at –195° and were then transferred for analysis.

Analysis. Gas chromatographic product analysis was made on a 100-ft Perkin-Elmer 0.02-in. support coated open tubular column, or with this column in series with a 300 ft × 0.01 in. squalane column at temperatures between 50 and 90°. The helium flow was split so that each column operated at its recommended flow rate. Calibrations were made with standard mixtures; product amounts were found to be proportional to the peak areas, corrected for carbon number.

Results

A particular H atom transfer will be described as an *Nab* process, where *N* is the ring size of the cyclic transition state, *a* = p, s, or t refers to a primary, secondary, or tertiary C–H bond being broken, and *b* = p, s, or t refers to the C–H bond being formed. Thus the isomerization of N1· to N5· is described as a 6sp reaction.

Reactions studied include 5ss, 6ss, 7ss, 5ps, 6ps, 7ps, 5sp, and 6sp. *Nab* processes with *N* < 5 are not important and may not occur as a simple transfer.⁷

Scavenging of Radicals. The steady-state concentration ratio of stabilized parent radicals relative to stabilized isomerized radicals, *S*/*S*_I, was obtained by use of radical getters G to trap out a portion of each radical as an unreactive paraffin product. The getters used were methyl or ethyl radicals which were generated *in*

(7) C. W. Larson and B. S. Rabinovitch, manuscript in preparation.

Table I. Results for the H + Hp3 Isomerization System Using a Methyl Radical Getter^a

Total pressure, mm	Mixture composition ^b		Relative product yields			S ₃ /S ₂	Hp3.* ^d /Hp4.*
	B1	H ₂	2MHpa	3MHpa ^c	4MHpa		
0.017	1.9	227	2	2	2	1	
0.070	1.6	227	17.0	28.0	45.4	1.65	0.99
0.13	1.8	227	15.4	44.4	59.8	2.88	1.00
0.22	0.3	227	16.5	55.0	75.3	3.34	0.95
0.45	1.9	227	12.9	71.0	90	5.50	0.93
0.78	0.6	960	7.05	61.4	70	8.7	0.98
1.28	0.3	1280	4.05	47.4	48.5	11.7	1.07
2.50	1.7	1090	2.7	72.0	69.0	27	1.09

^a Octane from heptyl-1· + Me was not observed in the 0.78-mm run where the minimum detectable amount was 5% of the 2MHpa. ^b Relative to *trans*-heptene-3 = 1.00. ^c An additional source of 3MHpa is from the *sec*-butyl + *n*-butyl combination; this source is negligible here because (sBu)_{ss} increases and (nBu)_{ss} decreases with increasing pressure such that the product (sBu)_{ss}(nBu)_{ss} ≪ (Me)_{ss}(Hp3·)_{ss}. ^d Hp3.* / Hp4.* = (Y(3MHpa) + Y(2MHpa))/Y(4MHpa).

situ from decomposition of chemically activated *sec*-butyl radicals (H + butene-1) or by stabilization of chemically activated ethyl radicals (H + ethylene). The steady-state concentration ratio was computed from the observed yields of recombination products, Y(R_p-G) and Y(R_I-G) (R_p = parent radical, R_I = isomerized radical), using the relation

$$(S/S_I) = \theta Y(R_p G) / Y(R_I G) \quad (1)$$

Since the sums of the rates of disproportionation and recombination for G + R_p and G + R_I are small and closely similar for the radicals of this study, the proportionality constant θ was taken to be unity in all cases.⁸

Individual Systems. A. Heptyl-3.* → Heptyl-2.*. Hp3.* was produced from *t*Hp3; an equal amount of Hp4.* was formed. The reaction of interest is Hp3·_{6ss} ⇌ Hp2·. The analysis of the C₈ alkanes from nine runs is summarized in Table I.

The proposal that the rates of H atom addition to each side of the double bond are equal was confirmed by the finding that the yields of alkanes from methyl trapping obeyed the relation

$$[Y(2MHpa) + Y(3MHpa)]/Y(4MHpa) \approx 1.0$$

at high (>0.07 mm of H₂) pressures (the abbreviation ending "a" signifies an alkane; e.g., 2MHpa is 2-methylheptane). Direct evidence for a net 6ps isomerization process, Hp3· → Hp1· (i.e., formation of *n*Oca), was not observed. An estimate of the upper limit for the total forward rate for the 6ps process may be obtained from the expression

$$k_a^{6ps} = R_Y / (1 - R_Y R_N)$$

where $R_Y = Y(\text{Oca})/Y(2\text{MHpa})$ and $R_N = k_a^{6sp}/k_a^{6ps}$. Depending upon the energy at which the radicals are effectively stabilized with respect to 6ps and 6sp processes, the theoretical value of R_N varies from ~9 to 13 at Hp3.* energies from 42 to 32 kcal mol⁻¹, respectively, and the net amount of Ocl· formed is insignificant. Using the values $R_Y < 0.05$ (footnote a, Table I) and $R_N \approx 11$, the upper limit to k_a^{6ps} may be established to be $\approx 9 \times 10^6$ sec⁻¹. The constant k_a^{5ps} for Hp4.* → Hp1.* is then estimated as $\sim 10^4$ sec⁻¹.

Figure 1 shows the dependence of $S/S_I \approx Y(3\text{MHpa})/Y(2\text{MHpa})$ on the hydrogen pressure. The behavior is as expected; at high pressures the slope approaches a constant value with a zero intercept (unit

slope on the log-log plot) which is equal to $(k_{a\infty}^{6ss})^{-1}$. Then $k_{a\infty}^{6ss} = 9.3 \times 10^5$ sec⁻¹.

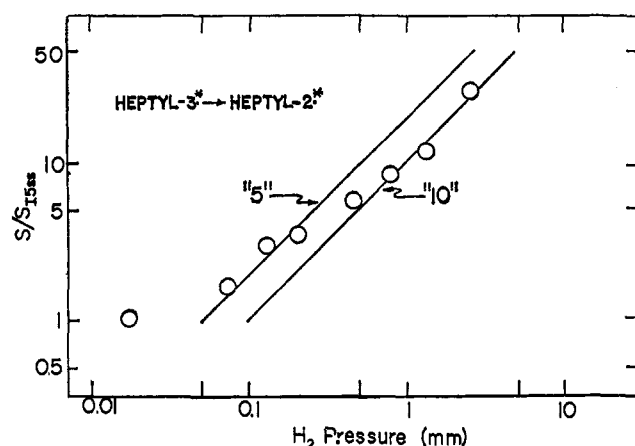
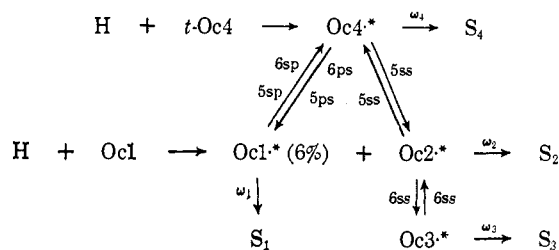


Figure 1. Isomerization of heptyl-3.* to heptyl-2.*; log-log plot of S/S_I vs. hydrogen pressure. The straight lines are of unit slope and correspond to lines of constant slope and zero intercept on a linear plot, with $k_{a\infty}^{6ss} = 5 \times 10^6$ and 10×10^6 sec⁻¹ as indicated ($\omega_{eff} = (1.0 \times 10^7$ sec⁻¹ mm⁻¹) P_{H_2} with use of an efficiency factor $\beta_{H_2} = 0.2$).

At lower pressures the slope is no longer constant due to the approach of equilibrium between Hp3.* and Hp2.*. Figure 1 is typical of all the isomerization systems studied. No attempt was made to construct a "theoretical curve" to account for the transition from high- to low-pressure behavior because only the high-pressure limit is useful for determining the isomerization rate constant, and such elaboration is not worthwhile.

B. Octyl Radical Isomerization. The octyl radical isomerization system is complicated by the participation of Oc1.*, Oc2.*, Oc3.*, and Oc4.* in a variety of interrelated isomerization reactions and quasi-equilibria. The system was approached from two directions by forming, in one case, Oc4.* and, in the other case, a mixture of 94% Oc2.* and 6% Oc1.*. The isomerization reactions are as follows.



(8) C. W. Larson and B. S. Rabinovitch, *J. Chem. Phys.*, **51**, 2293 (1969).

Table II. Results for the H + *t*Oc4 Isomerization System Using a Methyl Radical Getter^a

Total pressure, mm	Mixture composition ^b		Relative product yield ^c			$S_4/(S_2 + S_3)$	S_4/S_2	S_2/S_3
	B1	H ₂	4MOca	2MOca	3MOca ^c			
0.008	2.4	240	10	6		0.8 ^d	1.7	1.0 ^d
0.015	4.9	240	16.5	9.5	7.3	0.98	1.74	1.30
0.030	2.2	240	44.9	19.6	14.1	1.34	2.29	1.39
0.075	1.8	240	126	19.0	19.2	3.30	6.64	1.0
0.095	4.7	240	26.4	4.8	4.8	2.6	5.5	1.0
0.215	1.0	240	100	6.7		7.5 ^d	15	1.0 ^d
0.51	1.0	580	122	5	5.3	11.9	25	1.0

^a No octyl-1· + methyl product (nonane) was observed. The minimum detectable amount was 30% of the 3MOca. ^b Relative to *t*Oc4 = 1.0. ^c An additional source of 3MOca is *s*Bu + *n*-pentyl, which is negligible. ^d To obtain these values the identity $S_2 = S_3$ was used with the measured S_2 yield.

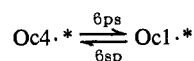
Table III. Results for the H + Ocl Isomerization System Using Methyl and Ethyl Radical Getters

Total pressure, mm	Methyl radical getter				Ethyl radical getter					
	Mixture composition ^a	H ₂	S_2/S_4	S_2/S_3	Total pressure, mm	Mixture composition	C=C	H ₂	S_2/S_4	S_2/S_3
0.031	3.9	248	1.81	1.57	0.11	10		84	2.80	1.80
0.070	3.7	240	2.33	1.42	0.21	6		84	1.30	1.40
0.084	1.3	160	2.04	1.36	3.40	11		315	12.2	1.81
0.125	2.6	213	3.8	1.00	7.20	17		550	14	1.97
0.200	0.07	122	4.1	1.00	14.1	14		860	12.8	2.22
0.195	0.4	135	2.8	1.00	28	13		1950	21.9	2.90
0.210	0.9	152	4.60	0.70	34	0		2700		12.7
0.20	3.1	220	4.4	1.2	63	14		455		160
2.0	0.1	127	6.5	0.8	96	0		7500		21.8
2.2	0.6	145	10.0	1.6	101	13		5700		310
4.5	4.5	400		1.69						
14.2	4.5	1300		3						
14.4	5.3	1180	15	7.2						
34	5.2	2700		7.8						
96	5.0	7500		8.5						

^a Relative to octene-1 = 1.00.

Relative concentrations of stabilized species were measured by using methyl or ethyl getters to trap out a portion of each radical. Results are listed in Tables II and III.

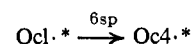
In the H + *t*Oc4 system, a net 6ps or 5ps process (to form Ocl·) was found to be unimportant. However, the amount of Ocl· isolated depends on the value of the equilibrium constants (R_N) for



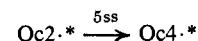
R_N is a function of the energy level so that the amount of Ocl· found depends on the energy level at which stabilization with respect to isomerization is effective. Since the difference between the heats of formation of Ocl· and Oc4· is ~ 4 kcal mol⁻¹, R_N varies from ~ 11 to ~ 16 when Oc4· is energized to a level of 38–32 kcal mol⁻¹, respectively. Thus, even if $k_{6\text{ps}}$ were greater than 10⁶ sec⁻¹, stabilized Ocl· would not have been detected.

Any Oc2·* formed by the 5ss process rapidly equilibrated (6ss) with Oc3·*; S_2/S_3 was unity over the lower pressure range studied (0.008 to 0.5 mm of H₂). This equilibration to Oc3·* was so fast that H₂ pressures greater than 10 mm were required to perturb it by collisional stabilization. At pressures where C–C decomposition is small, the net amount of Oc4·* isomerized is given by $I = S_2 + S_3$. From a plot of $(S_2 + S_3)/S_4$ vs. P_{H_2} the value of $k_{6\text{ss}}$ was determined, viz., $k_{6\text{ss}}(\text{Oc4}\cdot) = 3 \times 10^5$ sec⁻¹.

In the H + Ocl system, Oc2·* is the major product and may isomerize by 5ss or 6ss processes. The 7ss process yields Oc2·* again and therefore could not be measured. The 6% of Ocl·* formed by anti-Markovnikov addition⁹ may isomerize by several processes. The 6sp process is estimated to be at least 50 times faster than the sum of the other processes. Therefore



is a very labile reaction which interferes with the study of



The observed ratio, S_2/S_4 , must be corrected by subtracting this 6sp contribution to S_4 ; for details see ref 10. The observed rate constant, $k_{6\text{ss}}(\text{Oc2}\cdot) = (8 \pm 4) \times 10^5$ sec⁻¹, is here found to be larger than $k_{6\text{ss}}(\text{Oc4}\cdot)$. This is accounted for by the fact that Oc2·* carries 2.68 kcal mol⁻¹ more excess vibrational energy than does the Oc4·*. Unfortunately, experimental error is such that the relative rates are only fixed approximately between the factors of 1.54 and from different aspects of the data.

The 6ss isomerization rate of Oc2·* was determined by plotting S_2/S_3 vs. P_{H_2} . For pressures up to 10 mm of H₂ the ratio is near unity. Thus, the 6ss process is very fast indeed; $k_{6\text{ss}}(\text{Oc2}\cdot) = (6 \pm 3) \times 10^7$ sec⁻¹.

C. Isomerization Processes in the H + 3MP1 System. Detailed analysis of the important alkanes ap-

(9) W. E. Falconer, B. S. Rabinovitch, and R. J. Cvetanović, *J. Chem. Phys.*, **39**, 40 (1963).

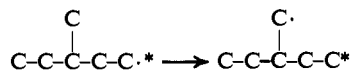
(10) C. W. Larson, Ph.D. Thesis, University of Washington, 1969.

Table IV. Results for the H + 3MP1 Isomerization System

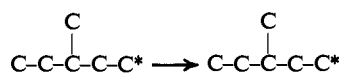
Total pressure, mm	Mixture composition ^a		3MHpa/3EtPa	23DMPa/33DMPa
	B1	H ₂		
0.28	3.7	175	>50	49
4.8	3.7	1000		>100

^a Relative to 3-methylpentene-1 = 1.0.

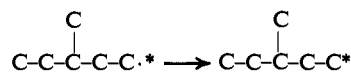
pears in Table IV. The following conclusions may be made. (a) 3MP1·* may isomerize by an inefficient 5pp process to 2EtB1·.



The ratio of methyl-trapped stabilization products, $Y(3\text{MHpa})/Y(3\text{EtPa})$, gave an upper limit for $k_{a\infty}^{5pp}(3\text{MP1}\cdot^*)$ as $1 \times 10^5 \text{ sec}^{-1}$. (b) The presence of 33DMPa in the products indicates that 3MP3·, formed from a net 3ts isomerization⁷ of 3MP2·*



was present. The 3ts process proceeds at about the same rate as the 5pp process, both being relatively unimportant (<2%) compared with ethyl rupture. (c) Analysis of 3MHa and 23DMPa products gave the upper limit for a 5sp process



as $k_{a\infty}^{5sp}(3\text{MP1}\cdot^*) < 10^6 \text{ sec}^{-1}$.

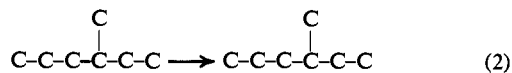
D. Isomerization Processes in the H + 3MH1 System. Product analysis is given in Table V. The

Table V. Results for the H + 3MH1 Isomerization System

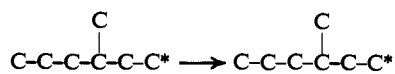
Total pressure, mm	Mixture composition ^a		S_2^b/S_5	S_2/S_3	$S_1/(S_2 + S_3)$
	B1	H ₂			
0.41	3.7	200	4.2	52	
0.83	3.3	200	5.2	38	0.01
1.10	3.7	200	6.2	56	0.02
2.00	1.1	200	9.3	70	0.02

^a Relative to 3-methylhexene-1 = 1.0. ^b $S_2 = 23\text{DMHa}$; $S_3 = 33\text{DMHa}$; $S_5 = 24\text{DMHa}$; $S_1 = 4\text{MHpa}$.

following is a summary of important conclusions. (a) 3MH2·* isomerizes by a 5ss process to 4MH2·*

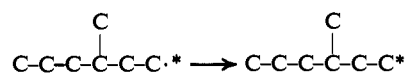


Study of this reaction is complicated by a subsequent decomposition.⁹ The rate $k_{a\infty}^{5ss}(3\text{MH2}\cdot^*)$ was estimated to be $1 \times 10^6 \text{ sec}^{-1}$. (b) The product of a (pseudo-) 3ts isomerization¹⁰ of 3MH2·* is 3MH3·*

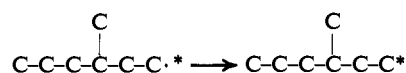


This rate relative to the 5ss process is about equal to the ratio of the methyl-trapped products $Y(24\text{DMHa})/Y-$

(33DMHa). This ratio is $\sim 1/8$ at all pressures, so $k_{a\infty}^{3ts}(3\text{MH2}\cdot^*) \sim 1.2 \times 10^5 \text{ sec}^{-1}$. (c) The 3MH1·* formed by nonterminal H atom addition to 3MH1 may isomerize by a 6sp process to 4MH2·*



Analysis is complicated by the fact that this is also the product of reaction 2, but, if one assumes 6% nonterminal addition,⁹ analysis of methyl-trapped products gives $k_{a\infty}^{6sp}(3\text{MH1}\cdot^*) > 4 \times 10^7 \text{ sec}^{-1}$. (d) A 5sp process



was not detected.

E. Nonyl Radical Isomerization. The excited nonyl-2 (N2·) radical may isomerize by 5ss, 6ss, and 7ss processes to form N5·*, N4·*, and N3·*, respectively. An 8ss process, if it occurred, would regenerate N2·* and would not be detectable. Analysis of C₁₀ alkanes is summarized in Table VI. (a) The 5ss prod-

Table VI. Results for the H + N1 Isomerization System^a

Total pressure, mm	Mixture composition ^b		S_2^c/S_5	S_2/S_4	S_2/S_3
	B1	H ₂			
0.10	1.9	210	3.9	1.4	1.8
0.14	1.9	250		1.3	1.8
1.2	3.5	740	46	2.2	8.0
17	8.1	7,700	>70	6.3	28
19	8.6	6,300	>60	4.0	
25	8.8	11,600	>200	8.0	50

^a *n*-Decane was never detected. The minimum detectable amount was about 2% of the 2-methylnonane. ^b Relative to nonene-1 = 1.00. ^c 5MNa yield has been corrected by assuming 6% nonterminal addition followed by a 6sp process.

uct (N5·*) can also arise by the 6sp isomerization of N1·* formed by nonterminal H atom addition to nonene-1. At and below 1 mm of pressure, this isomerization is certainly almost complete; the lower pressure data for N5· production by a 5ss process have been corrected by assuming 6% nonterminal addition; then $k_{a\infty}^{5ss}(N2\cdot^*) = 4 \pm 2 \times 10^5 \text{ sec}^{-1}$. (b) Analysis of the methyl-trapped N4· gave $k_{a\infty}^{6ss}(N2\cdot^*) = 4 \pm 1 \times 10^7 \text{ sec}^{-1}$. (c) Experimental error was such that $k_{a\infty}^{7ss}(N2\cdot^*)$ could only be roughly measured to between 1.7 and $6 \times 10^6 \text{ sec}^{-1}$.

F. Summary. A compilation of relative rate data on isomerization of alkyl radicals is presented in Table VII. Where possible, rates of competitive isomerization are given relative to the 5ss process set equal to unity; comparison is also made with the rate of C-C rupture.

Discussion

As Table VII demonstrates, a radical which has a reasonable isomerization pathway (*i.e.*, $N \geq 5$) available will almost certainly undergo such isomerization. In most cases isomerization is the fastest process which occurs.

Table VII. Summary of Relative Isomerization Rates

R_p^*	E_{\min}^a kcal	5sp	5ss	5pp	6sp	6ps	6ss	7ss	C-C rupture	
									Principal process and absolute rate, 10^5 sec^{-1}	
Hp3·	37.5		1 (7.5) ^b			<1.0 (<7.5)			B1 + <i>n</i> Pr·	1.2
Oc4·	37.5		1 (2.1)						H1 + Et·	0.14
Oc2·	40.5		1 (8)				75 (600)		Pr1 + P1·	1.0
N2· ^c	40.5		1 (20)				100 (2000)	5 (100)	Pr1 + H1·	0.09
Oc1· ^c	38.5				(>300) ^d				Ethylene + H1·	1.0
3MP1· ^c	39.5	(<0.5)		(<0.05)					Ethylene + <i>s</i> Bu·	20
3MH2·	39.5		(2.5)						<i>i</i> B2 + <i>n</i> Pr·	4.0
3MH1· ^c	37.5				(>100)				Ethylene + P2·	10
33DMH2·	39.5		(7.0)						2MB2 + <i>n</i> Pr·	2.3
33DMH1· ^c	37.5				(>200)				Ethylene + 2MP2·	4.0

^a E_{\min} is the minimum excess energy above the zero point level of the radical formed in the H + olefin activation step. ^b Numbers in parentheses are rates relative to the fastest C-C rupture process specified in the last column. ^c C-C rupture rates are estimated values; they are based on known related quantities and are probably correct to within a factor of 2. ^d Since, at equivalent energies, the 6sp for Oc1·* is at least as large as the 6ss of Oc2·*, this limit may be established by applying the appropriate correction to account for the lesser energy content of Oc1·*.

Comparison with Earlier Results. Some of the present results contradict earlier work¹¹ reported from this laboratory. Specifically, in a study of the decomposition rates of an homologous series of 2-alkyl radicals from C₄ to C₈ to give propylene in each case, it was concluded that none of the radicals isomerized to a significant extent. A partial explanation for this discrepancy is the improvement in our present analytical technique for the identification of trapped isomerization products. Fortunately, application of our present knowledge of isomerization processes to the older data reveals a silver lining.

First, it should be noted that 2-butyl radicals do not isomerize. 2-Pentyl radicals can isomerize by a 5sp process but this endothermic process is insignificant in net amount in these systems. 2-Hexyl (H2·) has two possible pathways: a 6ps process produces H1·* and is also insignificant in net amount because of its endothermicity, while a more labile 5ss process only reproduces the parent H2·*.

Hp2·* has two thermoneutral pathways, a dominant 6ss process which regenerates Hp2·*, and a 5ss process which yields Hp3· which, upon decomposition, does not produce propylene. This isomerization rate may be computed from that measured (Table VII) for the reverse reaction by taking into account the fact that Hp2·* from H + heptene-1 is 3.0 kcal mol⁻¹ more energetic than Hp3·* formed from H + *trans*-heptene-3 $k_{a\infty}^{5ss}(\text{Hp2}\cdot^*) = 18 \times 10^5 \text{ sec}^{-1}$, because at low pressures $(\text{Hp3}\cdot^*)/(\text{Hp2}\cdot^*) \sim 1$. Now in the earlier work, the yield of propylene was used to determine the amount of decomposition of Hp2·*. When the effect of the isomerization on the observed rate of decomposition of Hp2·* is considered, it is found to become important at lower pressures ($S/D < 60$) and is negligible above. A correction of the older heptyl data for this process which removes Hp2·* now eliminates a puzzling drop in the experimental rate constants at lower pressures ($S/D < 60$) and brings all these lower experimental points close to the calculated curve. However, the recorded high-pressure rate constant for decomposition $k_{a\infty}(\text{Hp2}\cdot)$ is only slightly affected; the recorded value $k_{a\infty} = 4.2 \times 10^5 \text{ sec}^{-1}$ now becomes $4.6 \times 10^5 \text{ sec}^{-1}$, and is in even better agreement with the theoretical value.

The 2-octyl system is more complicated and displays two thermoneutral isomerization pathways (5ss and 6ss) which remove Oc2·* and do not produce propylene upon decomposition. At all pressures studied, Oc2·* and Oc3·* are in equilibrium by a 6ss isomerization and on this account, therefore, all the earlier experimental decomposition rates for Oc2·* are low by a factor of 2. It is indeed found by Pearson and Rabinovitch¹¹ that the rate constant for decomposition $k_{a\infty}(\text{Oc2}\cdot)$ was, inexplicably, only approximately one-half of the theoretical value. In addition, the 5ss isomerization to Oc4·* can now be appraised to be of significant magnitude at the lowest pressures, but minor at the higher pressures. Correction of the earlier experimental rate constants for 2-octyl decomposition now brings the measured points to within 15% of the theoretical value: $k_{a\infty}(\text{exptl}) = 11 \times 10^4 \text{ sec}^{-1}$ and $k_{a\infty}(\text{calcd}) = 9.93 \times 10^4 \text{ sec}^{-1}$.

A Factor for Radical Isomerizations

Endrenyi and LeRoy⁵ have reported an unusually low preexponential factor of $1.4 \times 10^7 \text{ sec}^{-1}$ for 1-pentyl 5sp thermal isomerization. Since the present work was completed, an *A* factor of $2 \times 10^7 \text{ sec}^{-1}$ has been reported for 1-hexyl 6sp isomerization by Watkins and Ostreko.¹² Both of these groups agree that these low *A* factors cannot be easily explained. Our own measurements and calculations lead us to this same conclusion.

These two thermal studies are actually not necessarily in as good agreement as first appears. Endrenyi and LeRoy reported an Arrhenius activation energy $E_a^{5sp} = 10.8 \text{ kcal mol}^{-1}$ for the 5sp process, while Watkins and Ostreko found $8.3 \text{ kcal mol}^{-1}$ for 6sp reaction. Since a strain energy of $\sim 6.5 \text{ kcal}$ is normally ascribed to a five-membered carbon ring relative to the six-membered ring,¹³ then acceptance of the value $E_a^{6sp} = 8.3 \text{ kcal}$ suggests that $E_a^{5sp} \sim 15 \text{ kcal mol}^{-1}$ could be a more plausible value; on this basis, A_{6sp} would then rise to $4.7 \times 10^8 \text{ sec}^{-1}$, to fit the given measured rate constants.

The observed *A* factors cannot be reconciled with the known entropy differences between open chain and cyclic five- and six-carbon hydrocarbons.^{12,14} We

(12) K. W. Watkins and L. A. Ostreko, *J. Phys. Chem.*, **73**, 2080 (1969).

(13) M. Hanack, "Conformation Theory," Academic Press, New York, N. Y., 1965, p 13.

(11) M. J. Pearson and B. S. Rabinovitch, *J. Chem. Phys.*, **42**, 1624 (1965).

have estimated the vibration frequencies for the 1,6-hexyl diradical on the basis of the *n*-hexane assignment.¹⁵ Together with the cyclohexane assignment,¹⁵ this information may be used to calculate ΔS for $\dot{C}-C-C-C-C-\dot{C} \rightarrow$ cyclohexane. On assuming free rotation of the terminal CH_2 groups, ΔS^\ddagger is calculated to be -18 eu at $400^\circ K$ which, when translated to the present problem, corresponds to an *A* factor of 2.8×10^9 sec^{-1} .

Our data are not directly suited to determination of activation energies and *A* factors. However, we have measured the variation of $k_{a\infty}^{5ss}$ with internal energy in the 5ss isomerization



An increase by a factor of at least 1.5 was cited above when the minimum energy of radicals was increased by 2.7 $kcal\ mol^{-1}$ from 38.4 to 41.1 $kcal\ mol^{-1}$. Theoretical RRKM calculations of the 5ss isomerization rates have been made earlier⁸ for alternative loose and tight models for the activated complex; each model dictates a particular value for the critical threshold energy E_0^{5ss} in order to fit the observed values of k_a at the experimental energies; when fitted to the present experiment, these calculations permit some deductions regarding the values of A^{5ss} and E_0^{5ss} . As is shown in Figure 2, the variation of k_a with energy is dependent on the assigned value of E_0^{5ss} . The curves show that, even assuming the lower limit of a factor of 1.5 for the variation in $k_{a\infty}^{5ss}$, a value of E_0^{5ss} of at least 15 $kcal\ mol^{-1}$ is required to fit the present data; such a threshold corresponds to an *A* factor of $\sim 10^{11}$ sec^{-1} and, to an even larger value of the minimum thermal activation energy, E_a^{5s} .

Role of Vibrational Excitation

It should be noted here that these unimolecular radical isomerizations involving cyclic transition states may have some relevance to the determination of the role of vibrational excitation in bimolecular reactions. An H atom transfer occurring internally in a long-chain mole-

(14) F. D. Rossini, "Selected Values of Physical and Thermodynamic Properties," Carnegie Press, Pittsburgh, Pa., 1953.

(15) J. H. Schachtschneider and R. G. Snyder, *Spectrochim. Acta*, **19**, 117 (1963); **21**, 169 (1965).

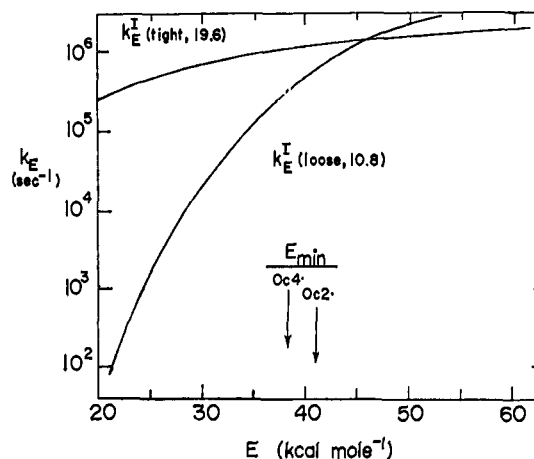


Figure 2. Dependence of k_E on E in the octyl-5ss isomerization systems for alternative values of E_0^I and concomitant entropies of activation. The activated complex models were chosen so that the average calculated rates fitted the observed rate for octyl-2·*. Energies are, $kcal\ mol^{-1}$, $E_{min}(Oc4\cdot) = 38.4$, $E_{min}(Oc2\cdot) = 41.1$, $E_0^I(Loose) = 19.6$, $E_0^I(tight) = 10.8$.

cule can be thought of as a "bimolecular" process between the two ends of the molecule with the relative "translation" being supplied by excited bending modes. This is to be compared with the conventional collisional model for the bimolecular abstraction process, $R\cdot + HR' \rightarrow RH + R'\cdot$; for this process, the exponential term in the Arrhenius equation is customarily assigned to the probability that the relative translational energy of colliding pairs parallel to the line of centers should exceed a required magnitude.

The excess energy of the radical resides simultaneously in many modes (including the rupturing C-H stretch). This, together with the fact that in this unimolecular system the reacting ends may make repeated encounters, obviously differentiates the unimolecular and bimolecular processes quite fundamentally. In any case, the analogies between the two should be kept in mind and the possibility remembered that systems of this and related kind may be useful in clarifying the role of internal vibrational excitation in bimolecular processes.