formation of a nonvolatile compound with some reactor material.

The appearance potentials of Kr^+ and KrF^+ were measured from -75 to $-50°$ using an extrapolated difference method involving plots of the ion intensity vs. the difference in ionizing electron energy for the unknown ion and some convenient standard ion that is necessary to produce equivalent ion intensities.[9] A typical such manipulation of the ionization efficiency data on KrF^+ appears in Figure 2. Eleven measurements were made on both $^{84}Kr^+$ and $^{84}KrF^+$ using argon as the standard, $I(Ar) = 15.76$ eV, and the results were $A(Kr^+, KrF_2) = 13.21 \pm 0.25$ eV, and $A(KrF^+, KrF_2) = 13.71 \pm 0.20$ eV.

Possible processes for the formation of Kr^+ from KrF_2 involve the formation of two F atoms, two F^- atoms, and one F and one F^- atom, or an F_2 molecule. The merits of each of these four processes were explored using $D_{av}(Kr-F) = 11.7$ kcal/mol, 0.51 eV, as calculated from the calorimetrically determined ΔH_f-(KrF_2),[10] $I(Kr) = 14.00$ eV, $EA(F) = 3.57$ eV, and $\Delta H_f(F) = 0.82$ eV. The latter of these four processes, i.e.

$$KrF_2 + e \longrightarrow Kr^+ + F_2 + 2e \qquad (1)$$

yields a predicted $A(Kr^+)$ of 13.4 eV which is in best agreement with experiment. If reaction of KrF_2 with reactor material were occurring at these low temperatures, as discussed above, then $A(Kr^+)$ would equal $I(Kr)$, which is not the case.

Similarly KrF^+ can be formed with either an F atom or an F^- ion. Neither of these processes can be verified since the ionization potential of the KrF radical is unknown, and there is no reason to believe that $D_{av}(Kr-F)$ closely equals $D(KrF-F)$. If one makes this assumption, however, F atom formation implies $I(KrF) = 13.20$ eV while F^- ion formation suggests $I(KrF) = 16.77$ eV. Instrumental deficiencies prohibited a study of the negative ion spectrum.

(9) J. W. Warren and C. A. McDowell, *Discussions Faraday Soc.,* **10,** 53 (1951).

(10) S. R. Gunn, *J. Phys. Chem.,* **71,** 2934 (1967).

Isomerization of n-Hexyl Radicals in the Gas Phase

by K. W. Watkins and L. A. Ostreko

Department of Chemistry, Colorado State University, Fort Collins, Colorado 80521 (*Received November 21, 1968*)

The isomerization of long-chain alkyl radicals *via* intramolecular hydrogen atom migration was first proposed by Kossiakoff and Rice[1] to explain the products observed from the decomposition of hydrocarbons.

Gordon and McNesby[2] found evidence for n-pentyl radical isomerization at 300° by observing the products propene and ethyl radical presumably from sec-pentyl radical decomposition. Quantitative kinetic data on radical isomerizations are lacking. Recently, Endrenyi and LeRoy[3] have reported kinetic parameters for the intramolecular 1–4 hydrogen atom migration in n-pentyl radical. n-Pentyl radicals were produced by the addition of n-propyl radicals to ethylene. The n-propyl radicals resulted from the addition of methyl radicals to ethylene. The detection of isohexane in the products was taken as evidence that some n-pentyl radicals had isomerized to sec-pentyl. sec-Pentyl radicals on combination with a methyl radical gave isohexane. The rate constant reported for the 1–4 intramolecular hydrogen atom migration was $k = 1.4 \times 10^7 \exp(-10.8 \times 10^3/RT)$ sec^{-1}.

In the course of a similar study of the kinetics of the addition of ethyl radicals to ethylene we have found evidence for the isomerization of n-hexyl radical to sec-hexyl radical. The rate constant for the unimolecular isomerization is similar to that reported for n-pentyl radical isomerization.

Experimental Section

Azoethane was prepared by the method of Leitch[4] and stored in the vapor phase in a blackened bulb. All gas handling was performed with a conventional vacuum system. Azoethane and ethylene were measured separately for each run. Azoethane at a concentration of about 0.5×10^{-6} mol cm^{-3} was photolyzed in the presence of about 2×10^{-6} mol cm^{-3} of ethylene. Unfiltered light from a Hanovia 550-W high-pressure mercury arc lamp was used for the irradiation. The reaction vessel was a 10.0-cc Pyrex cylinder. The amount of azoethane consumed was usually between 15 and 25%, and the ethylene consumed was always less than 1% of the initial ethylene.

After an irradiation time of either 4 or 8 min the entire reactant–product mixture was analyzed by gas chromatography, using a 6-ft silica gel column and a flame ionization detector. Quantitative determinations were based on calibrations of peak areas using measured amounts of certain hydrocarbon standards. The use of hydrocarbon standards containing varying numbers of carbon atoms showed that the response (peak area) per mole of hydrocarbon was directly proportional to the number of carbon atoms per molecule.
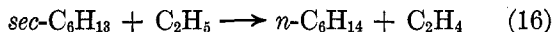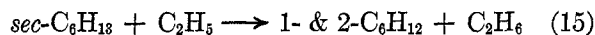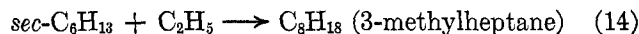
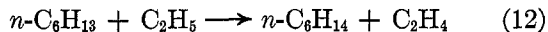### Results and Rate Constant Calculation

Reactions 1–16 were proposed to explain the observed products.

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

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

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

(4) R. Renaud and L. C. Leitch, *Can. J. Chem.,* **32,** 545 (1954).

$$C_2H_5N_2C_2H_5 + h\nu \longrightarrow 2C_2H_5 + N_2 \qquad (1)$$

$$C_2H_5 + C_2H_4 \longrightarrow n\text{-}C_4H_9 \qquad (2)$$

$$2C_2H_5 \longrightarrow n\text{-}C_4H_{10} \qquad (3)$$

$$2C_2H_5 \longrightarrow C_2H_4 + C_2H_6 \qquad (4)$$

$$n\text{-}C_4H_9 + C_2H_5 \longrightarrow n\text{-}C_6H_{14} \qquad (5)$$

$$n\text{-}C_4H_9 + C_2H_5 \longrightarrow 1\text{-}C_4H_8 + C_2H_6 \qquad (6)$$

$$n\text{-}C_4H_9 + C_2H_5 \longrightarrow n\text{-}C_4H_{10} + C_2H_4 \qquad (7)$$

$$n\text{-}C_4H_9 + C_2H_4 \longrightarrow n\text{-}C_6H_{13} \qquad (8)$$

$$2n\text{-}C_4H_9 \longrightarrow n\text{-}C_8H_{18} \qquad (9)$$

$$2n\text{-}C_4H_9 \longrightarrow 1\text{-}C_4H_8 + n\text{-}C_4H_{10} \qquad (9a)$$

$$n\text{-}C_6H_{13} + C_2H_5 \longrightarrow n\text{-}C_8H_{18} \qquad (10)$$

$$n\text{-}C_6H_{13} + C_2H_5 \longrightarrow 1\text{-}C_6H_{12} + C_2H_6 \qquad (11)$$

$$n\text{-}C_6H_{13} + C_2H_5 \longrightarrow n\text{-}C_6H_{14} + C_2H_4 \qquad (12)$$

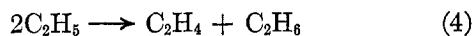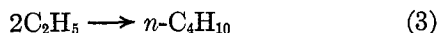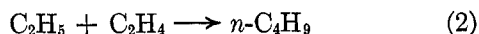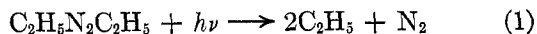$$n\text{-}C_6H_{13} \longrightarrow sec\text{-}C_6H_{13} \qquad (13)$$

$$sec\text{-}C_6H_{13} + C_2H_5 \longrightarrow C_8H_{18} \ (3\text{-methylheptane}) \qquad (14)$$

$$sec\text{-}C_6H_{13} + C_2H_5 \longrightarrow 1\text{- \& 2-}C_6H_{12} + C_2H_6 \qquad (15)$$

$$sec\text{-}C_6H_{13} + C_2H_5 \longrightarrow n\text{-}C_6H_{14} + C_2H_4 \qquad (16)$$

The competition between n-hexyl combination with ethyl and n-hexyl isomerization was used to calculate the rate constant for isomerization

$$\frac{R_{13}}{R_{10}} = \frac{R(sec\text{-hexyl products})}{R(n\text{-octane})_{10}} = \frac{k_{13}[C_2H_5][n\text{-hexyl}]}{k_{10}[C_2H_5][n\text{-hexyl}]} \qquad (i)$$

where R refers to the rate of formation of the product in mol cc^{-1} sec^{-1}. Assuming that sec-hexyl radical reacts predominantly with ethyl radical by reactions 14, 15, and 16

$$R(sec\text{-hexyl products}) =$$
$$\frac{k_{14} + k_{15} + k_{16}}{k_{14}} R(3\text{-methylheptane}) \qquad (ii)$$

The cross disproportionation to combination ratios, k_{15}/k_{14} and k_{16}/k_{14}, could not be measured accurately, and so they were estimated. The ratio k_{15}/k_{14} was estimated to be ~0.25 from the ratio of R(hexene)/R(3MH) in runs where n-hexyl concentration was much less than sec-hexyl. The ratio k_{16}/k_{14} was estimated to be $^3/_5$ of k_{15}/k_{14} on the basis of the number of hydrogen atoms available for disproportionation. Thus, $k_{16}/k_{14} \simeq 0.15$. Further substantiation for k_{16}/k_{14} comes from a comparison to the value for the ethyl–isopropyl cross disproportionation to combination ratios where H is transferred from ethyl to isopropyl; that value was reported to be 0.19.[5]

The octane produced in reaction 10 was found by subtracting the octane found in reaction 9 from the total octane. $R(n\text{-octane})_{10} = R(n\text{-octane}) - R(\text{octane})_9$, where $R_9 = k_9[n\text{-}C_4H_9]^2$, which on sub-

stitution of $[n\text{-}C_4H_9] = R(C_6H_{14})/k_5[C_2H_5]$ and $[C_2H_5] = R^{1/2}(C_4H_{10})/k_3^{1/2}$ yields

$$R_9 = \frac{k_3k_9}{k_5^2} \frac{R^2(C_6H_{14})}{R(C_4H_{10})} \qquad (iii)$$

In the derivation of (iii) it was assumed that $R_3 = R(C_4H_{10}) = k_3[C_2H_5]^2$, and $R_5 = R(C_6H_{14}) = k_5[C_2H_5] \cdot [C_4H_9]$. This assumption is justified as follows. From the rates of formation of products (Table I), and the

Table I: Isomerization of n-C$_6$H$_{13}$[a]

Run	T, °K	n-C$_8$H$_{18}$	3-MH	n-C$_6$H$_{14}$	n-C$_4$H$_{10}$	$(k_{13}k_3^{1/2}/k_{10}) \times 10^5$
8	352.2	0.52	0.29	18.0	254	3.2
9	354.4	0.44	0.31	13.1	144	3.7
10	354.7	0.70	0.43	18.4	265	2.6
11	354.7	0.36	0.22	15.1	229	4.2
13	383.2	2.16	2.11	35.6	206	6.7
14	385.7	2.70	2.73	43.5	243	7.8
16	396	3.33	3.94	44.2	189	10.1
17	396.7	3.12	3.75	40.3	154	13.6
18	399.7	2.40	3.24	36.3	166	13.9
19	404.7	3.06	3.82	45.0	196	16.3
15[b]	387.7	2.12	2.34	32.9	169	8.2
21[c]	388	1.70	1.88	24.7	112	8.2

[a] Rates of formation of products are in mol cm^{-3} sec^{-1} $\times$ 10^{12}. [b] 18.4 $\times$ 10^{-6} mol cm^{-3} of Xe added. [c] 4.70 $\times$ 10^{-6} mol cm^{-3} of C$_8$F$_8$ added.

estimated ratios $k_{12}/k_{10} = 0.10$ and $k_{16}/k_{14} = 0.15$, the contribution to $R(C_6H_{14})$ from R_{12} and R_{16} is only 0.4% at 352°K and 1.4% at 404°K. Similarly the contribution to $R(C_4H_{10})$ by R_7 and R_{9a}, using the ratios $k_7/k_5 = 0.09$ and $k_{9a}/k_9 = 0.14$, can be shown to be less than 1% at 352°K and 2.2% at 404°K. Therefore over 98% of the n-butane and n-hexane is produced in reactions 3 and 5, respectively. According to simple collision theory, the ratio k_3k_9/k_5^2 is equal to $^1/_4$ for reactions with no activation energy. Most of the available data are in agreement with this prediction.[5]

Expression i becomes

$$\frac{k_{13}}{k_{10}} = \frac{1.4R(3\text{-methylheptane})[C_2H_5]}{R(n\text{-octane})_{10}} \qquad (iv)$$

and after substitution of $[C_2H_5] = R^{1/2}(C_4H_{10})/k_3^{1/2}$

$$\frac{k_{13}k_3^{1/2}}{k_{10}} = 1.4\frac{R(3\text{-methylheptane})}{R(n\text{-octane})_{10}} R^{1/2}(C_4H_{10}) \qquad (v)$$

In this development the reverse reaction sec-hexyl → n-hexyl was neglected. Values of k_{13}/k_{-13} are not available, but a reasonably accurate estimate can be made. The estimate is the same as that made by Endrenyi and LeRoy.[3] Thus it will not be presented

(5) J. A. Kerr and A. F. Trotman-Dickenson, *Progr. Reaction Kinetics*, **1**, 105 (1961).
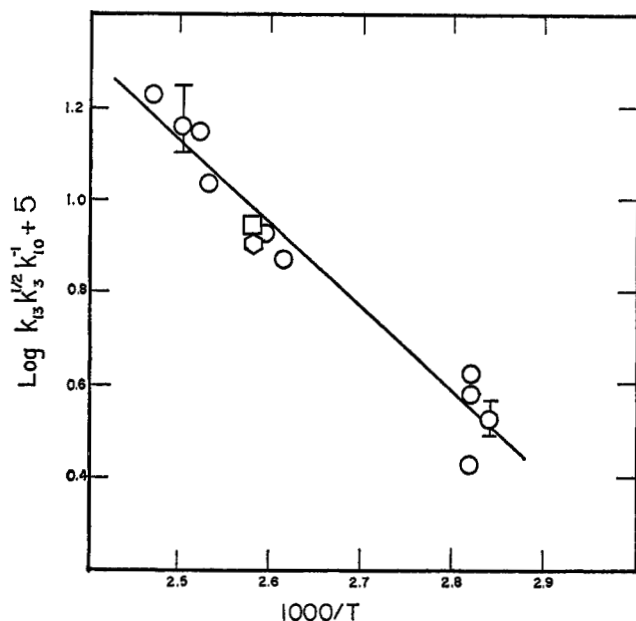
Figure 1. Arrhenius plot for the isomerization of n-hexyl radicals; O, C_3F_8 added; □, Xe added.

here. From the calculated equilibrium constant K_{13}, k_{13}/k_{-13} ranges from 1.2×10^3 to 4.5×10^2 over the temperature range 350 to 410°K.

The values of $k_{13}k_3^{1/2}/k_{10}$ obtained from expression v are given in Table I, and in Arrhenius form in Figure 1. A least-squares calculation gave $E_{13} + {}^1/_2E_3 - E_{10} = 8.3 \pm 1.7$ kcal/mol and $\log A_{13}A_3^{1/2}/A_{10} = 0.64$. The relatively large error is introduced by the quantity R_{10} which is much smaller than $R(n\text{-octane})$.

The activation energies E_3 and E_{10} for alkyl radical combination reactions were assumed to be essentially zero; thus $E_{13} = 8.3$ kcal/mol. To calculate the preexponential factor A_{13}, it was necessary to assume $A_8 = A_3 = 2.2 \times 10^{13}$ mol^{-1} cc sec^{-1}, since A_8 has not been reported in the literature.[6] Therefore, $A_{13} = 10^{7.30\pm1.0}$ sec^{-1}. The rate constant is $k_{13} = 2.0 \times 10^7 \cdot \exp(-8.3 \times 10^3/RT)$ sec^{-1}.

Discussion

The 1–5 hydrogen atom migration in n-hexyl radical is an intramolecular analog of the bimolecular reaction

$$R + R'H = RH + sec\text{-}R'$$

For the case where R is an ethyl radical and R'H is a hydrocarbon, ketone, or azoethane, the activation energy is often found to be between 7.5 and 8.7 kcal/mol.[5] Endrenyi and LeRoy found $E = 10.8$ kcal/mol for the 1–4 hydrogen atom migration in n-pentyl and attributed the increase of ~2.5 kcal/mol in activation energy above that for an intermolecular hydrogen abstraction as being due to strain energy (Pitzer and Baeyer strain) on forming the five-membered ring, activated complex. The value of 8.3 kcal/mol re-

ported here for the activation energy for n-hexyl isomerization is consistent with the estimate of essentially zero strain energy for a six-membered ring, activated complex.[7,8]

For n-pentyl and n-hexyl isomerization, the preexponential factors are 1.4×10^7 and 2.0×10^7 sec^{-1}, respectively. In terms of activated complex theory, assuming the transmission coefficient to be unity, the entropy of activation, $\Delta S^{\ddagger}$, at 400°K would have to be -28 eu for n-hexyl isomerization. These are possibly the lowest reliable preexponential factors found for a unimolecular reaction.[9] It is important to be certain of the mechanism. A factor worth considering was the influence of vibrationally excited n-hexyl radicals.

When the n-hexyl radical is first formed by the addition of n-butyl to ethylene, it contains mostly as vibrational energy the ΔE of reaction (22.8 kcal/mol) plus E, the activation energy for addition. This is some 30 kcal/mol greater than that of an average thermal n-hexyl radical at 100°. Since the activation energy barrier for isomerization via hydrogen atom migration is only about 8 kcal/mol, the chemically activated radical has sufficient energy to isomerize, unless deactivated by collision. To answer the question of whether or not the chemically activated n-hexyl radical was responsible for the isomerization, we carried out two runs in which an excess of an "inert" gas was added. Xenon and C_3F_8 were used. In one experiment a sevenfold excess of Xe was added compared to the reactants C_2H_4 and azoethane, and in the other experiment a twofold excess of C_3F_8 was added to increase the stabilization (collision) rate. The calculated rate constants for isomerization were unaffected by the increase in pressure (Figure 1), which means that even without the addition of inert gases the chemically activated n-hexyl radical is stabilized before isomerization. Therefore, the radicals undergoing isomerization are in thermal equilibrium with the bath.

We can now return to the question of the "low" preexponential factor. In the work on n-pentyl isomerization, the authors concluded that the removal of internal rotation alone could not account for the entropy of activation since this is usually less than 5 eu per internal rotation. They suggested that to treat the A factor in terms of transition-state theory, it was necessary to assume that the transmission coefficient (κ) is much less than unity. Laidler[10] points out two classes of reaction for which the coefficient may be considerably

(6) A_3 is the association constant for methyl radicals; A. Shepp, *J. Chem. Phys.*, **24**, 939 (1956).

(7) M. Hanack, "Conformation Theory," Academic Press, New York, N. Y., 1965, p 44.

(8) The strain energy of zero is actually for the chair form of cyclohexane; the six-membered ring activated complex for isomerization would of course have a hydrogen atom in the ring.

(9) H. E. O'Neal and S. W. Benson, *J. Phys. Chem.*, **71**, 2903 (1967).

(10) K. J. Laidler, "Chemical Kinetics," McGraw-Hill Book Co., Inc., New York, N. Y., 1965, p 80.

less than unity. The first comprises atom and small radical combination in the gas phase. When atoms and small radicals combine, the resulting molecule contains, largely as vibrational energy, the energy of the new bond. The vibrationally excited molecule will dissociate to reactants if it is not stabilized. Therefore, not all activated complexes become products and κ is less than unity. The second case is for reactions where there is a change from one type of electronic state to another. The second case is not applicable here. Consider, further, the first case. At the instant a sec-hexyl radical is formed it contains the ΔE of reaction (~ 5 kcal/mol, the difference between the energy of a primary and a secondary C–H bond) plus the activation energy for isomerization mostly as excess vibrational energy. As in the case of small atom recombination, if collisional deactivation does not occur the sec-C_6H_{13} radical can pass back over the energy barrier at some specific rate to form n-C_6H_{13}. If passage back over the barrier is competing favorably with deactivation, then the effect of an added "inert" gas should be to increase the relative yield of sec-hexyl radicals (and hence the measured rate constant). Since the runs with added Xe and C_3F_8 showed no effect on the measured rate constant for isomerization, we conclude that there is no return of excited sec-C_6H_{13} radicals to n-C_6H_{13}. Without evidence for the participation of vibrationally excited species, it is difficult to understand why the transmission coefficient can be less than unity.

For n-hexyl radical isomerization, as was the situation for n-pentyl, the loss of internal rotation alone cannot account for $\Delta S^{\ddagger}$. At 298°K, $\Delta S^{\ddagger} = 27$ eu. To estimate the entropy loss per internal rotation, we can compare the entropies of cyclohexane and n-hexyl radical[11] and divide the difference by the number of internal rotations, i.e., five. Thus $S°$(cyclohexane) $-$ $S°$(hexyl) $= (71.3) - (95.2) = -23.9$ eu, or 4.8 eu per rotation. Since four internal rotations are "frozen" on forming the activated complex for hexyl radical isomerization, loss of internal rotation alone accounts for 19.2 of the 27 eu.

O'Neal and Benson[9] have been able to account for the A factors of many four- and six-centered unimolecular elimination reactions using activated complex theory. They proposed the use of "loose" cyclic activated complexes. These are structures with weak interactions at the reacting "ends." However, for intramolecular hydrogen atom migration, the end interactions are quite strong due to the partial bonding of the hydrogen atom to both "ends." In this case some of the force constants of the low-frequency bending vibrations of the open-chain radical are increased in the activated complex. This contributes a lowering of the entropy in addition to that from loss of internal rotation. These structures correspond to "tight" cyclic activated complexes.

(11) J. G. Calvert and J. N. Pitts, Jr., "Photochemistry," John Wiley & Sons, Inc., New York, N. Y., 1966, p 815.

The Rate of Hydrogen Abstraction by CF₃· and C₂F₅· in Liquid Cyclohexane[1]

by Pierre P. Infelta and Robert H. Schuler

Radiation Research Laboratories, Mellon Institute, Carnegie-Mellon University, Pittsburgh, Pennsylvania 15213
(Received November 25, 1968)

Alkyl radicals are produced in the radiolysis of hydrocarbon solutions of organic halides by dissociative electron capture[2] and as a result reactions such as $CF_3Br + e^- \rightarrow CF_3\cdot + Br^-$ can serve as a convenient source of fluorinated radicals for kinetic studies. During the course of investigations on electron capture by perfluoroalkyl bromides and chlorides[3] the scavenging of the perfluoroalkyl radicals *via*

$$CF_3\cdot + I_2 \xrightarrow{k_1} CF_3I + I\cdot \qquad (1)$$
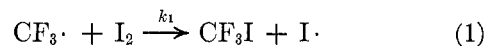
was found to be incomplete at iodine concentrations of $\sim 10^{-4}$ M. Presumably competitive abstraction of hydrogen from the solvent (reaction 2) occurs. In the

$$CF_3\cdot + RH \xrightarrow{k_2} CF_3H + R\cdot \qquad (2)$$

vapor phase the collision efficiency of reaction 1 is known to be very high[4] and accordingly it is reasonable to assume that in the liquid phase the scavenging reaction proceeds at or near to the diffusion-controlled limit (as it also does in the case of $CH_3\cdot$[5]). We wish to report here briefly measurements of the rate constant ratio k_2/k_1 which, together with the above assumption, show that in liquid cyclohexane the rate of reaction 2 is two to three orders of magnitude greater than that for abstraction of hydrogen by methyl radicals. This result thus parallels the conclusions from vapor-phase experiments where the abstraction reactions of $CF_3\cdot$ radicals are found to have relatively low activation energies.[6]

(1) Supported in part by the U. S. Atomic Energy Commission.
(2) J. M. Warman, K.-D. Asmus, and R. H. Schuler, *J. Phys. Chem.*, in press.
(3) P. P. Infelta and R. H. Schuler, to be submitted for publication.
(4) J. C. Amphlett and E. Whittle, *Trans. Faraday Soc.*, **62**, 1662 (1966), estimated the rate constant for reaction 1 to be 2.6 × 10⁹ M^{-1} sec⁻¹.
(5) R. H. Schuler and R. R. Kuntz, *J. Phys. Chem.*, **67**, 1004 (1963).
(6) See Table XII of the review article by A. F. Trotman-Dickenson, *Advan. Free-Radical Chem.*, **1**, 26 (1965), for a summary of available rate information on the reactions of fluorinated alkyl radicals.