occur to the $^3(\pi,\pi^*)$ state with resulting cis–trans isomerization. It is therefore not surprising that the intersystem crossing rate constant for AIP is greater than the corresponding constants for DBO and DBH, being in excess of 10^{10} sec^{-1}.[1] For bicyclic azo compounds, the lower intersystem rate constants may be understood in terms of a crossing to a (n,π^*) rather than a (π,π^*) manifold[38] and less marked differences between the equilibrium geometries of the states, resulting in less favorable Franck–Condon factors.[35]

In this previous work we have used sensitization extensively as a source of triplet molecules.[1,7] In Table I the interaction rate constante (k_{ir}) of a variety of substrates, including azo compounds, with several triplet donors are recorded. However, these constants are specifically values required for the estimation of triplet lifetimes and are neither for a systematic group of acceptors nor designed to study the variations in k_{ir} *per se.* One of us has recently reported on the factors influencing the rates of singlet–singlet energy transfer involving aliphatic azo compounds,[12] and we are now in the process of expanding the number and type of triplet donors and quenchers listed in Table I in order to establish patterns of triplet quenching. It is hoped in this way to obtain a better understanding of the factors involved in triplet–triplet energy transfer.

Acknowledgment. We are grateful to the National Science Foundation (Grant No. GP-18808) for support of this work.

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Photolysis of *n*-Pentylazomethane Vapor. Reactions of the *n*-Pentyl Radical[1]

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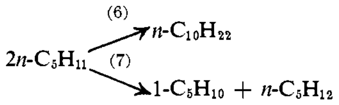
Abstract: The vapor-phase photolysis of *n*-pentylazomethane was studied in the temperature range 24–162°. The product rate data fit well the proposed reaction scheme involving methyl and *n*-pentyl radicals. Evidence for the generation of photochemically activated *n*-pentyl radicals was found. The implications of this evidence to previous work on the photolysis of azoalkanes are discussed. When the concentration of photochemically activated radicals was minimized, the thermal rate constants for the isomerization and H-atom abstraction reactions of the *n*-pentyl radical were determined: $n\text{-C}_5\text{H}_{11} \rightarrow sec\text{-C}_5\text{H}_{11}$ (17), $k_{17} = 3.3 \times 10^8 \exp(-15.1 \times 10^3/RT)$ sec^{-1}; $n\text{-C}_5\text{H}_{11} + n\text{-C}_5\text{H}_{11}\text{N}_2\text{CH}_3 \rightarrow n\text{-C}_5\text{H}_{12} + \text{C}_5\text{H}_{10}\text{N}_2\text{CH}_3$ (20), $k_{20} = 4.2 \times 10^{11} \exp(-7.8 \times 10^3/RT)$ mol^{-1} cm^3 sec^{-1}. The disproportionation to combination ratio at 25° for *n*-pentyl radicals was estimated to be 0.14, and $\Delta(\text{Me}, n\text{-Pe}) = 0.033$.

There is almost no quantitative information in the literature on the reactions of the *n*-pentyl free radical. Only one estimate of the disproportionation to combination ratio has been reported.[2] The data obtained by Wijnen from his study of the photolysis of 2-heptanone vapor gave a value of ~0.2 for k_7/k_6 at 63°.



$$2n\text{-C}_5\text{H}_{11} \xrightarrow{(6)} n\text{-C}_{10}\text{H}_{22}$$
$$2n\text{-C}_5\text{H}_{11} \xrightarrow{(7)} 1\text{-C}_5\text{H}_{10} + n\text{-C}_5\text{H}_{12}$$

Of special interest is the isomerization of *n*-pentyl radicals *via* a 1,4 hydrogen-atom transfer. Wijnen observed products from the *sec*-pentyl radical and suggested that they resulted from isomerization of *n*-pentyl. He did not measure a rate constant. Isomerization of C_5, C_6, and C_7 alkyl radicals is well documented,[3] but the activation energies and *A* factors are only known as estimates. Recently the Arrhenius parameters of the only two reported rate constants[4,5] for isomerization of alkyl radicals have been shown to be uncertain.[6]

Rabinovitch and coworkers[7] have studied the unimolecular isomerization of ten different vibrationally excited alkyl radicals. While no activation energy was measured, their theoretical RRKM calculations for 5_{ss} isomerization rates fitted the experimental rate constant best when the threshold energy for isomerization was ~15 kcal mol^{-1}. According to the notation of Rabinovitch,[7] the 1,4 H-atom transfer for *n*-pentyl would be a 5_{sp} process, indicating a five-membered ring activated complex in which a secondary C–H bond is broken and a primary C–H bond is formed.

The present work was initiated to obtain more reliable kinetic data on *n*-pentyl radical reactions. A clean source of *n*-pentyl radicals was needed. In view of the extensive work of Calvert and coworkers[8] who used the photolysis of azoalkanes as clean alkyl radical sources, the photolysis of 1,1′-azo-*n*-pentane was expected to be

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[1] Presented at the Midwest Regional Meeting of the American Chemical Society, Lincoln, Neb., 1970, No. 622.

[2] M. H. J. Wijnen, *J. Amer. Chem. Soc.*, **83**, 3752 (1961).

[3] (a) H. M. Frey and R. Walsh, *Chem. Rev.*, **69**, 103 (1969); (b) D. A. Leathard and J. H. Purnell, *Annu. Rev. Phys. Chem.*, **21**, 197 (1970); (c) S. W. Benson, "Thermochemical Kinetics," Wiley, New York, N. Y., 1968, p 164.

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[5] K. W. Watkins and L. A. Ostreko, *ibid.*, **73**, 2080 (1969).

[6] K. W. Watkins and D. R. Lawson, *ibid.*, **75**, 1632 (1971).

[7] E. A. Hardwidge, C. W. Larson, and B. S. Rabinovitch, *J. Amer. Chem. Soc.*, **92**, 3278 (1970).

[8] (a) J. A. Kerr and J. G. Calvert, *ibid.*, **83**, 3391 (1961); (b) W. E. Morganroth and J. G. Calvert, *ibid.*, **88**, 5387 (1966); (c) D. H. Slater, S. S. Collier, and J. G. Calvert, *ibid.*, **90**, 268 (1968).

a suitable source of *n*-pentyl radicals. Instead, *n*-pentylazomethane was selected because its vapor pressure is higher than that of azopentane. While methyl radicals are also generated, they do not cause undue complications.

Experimental Section

n-Pentylazomethane (PAM), a compound not reported in the literature, was synthesized by a procedure similar to that used in the preparation of symmetrical azoalkanes.[9] Equivalent amounts of *n*-valeraldehyde and methylhydrazine were allowed to react in ether solvent to produce $CH_3(CH_2)_3CHN_2HCH_3$, bp 152°. This compound was reduced with $LiAlH_4$ to yield 1-*n*-pentyl-2-methylhydrazine, bp 149°. The 1,2-dialkylhydrazine was then oxidized with HgO to yield the desired product, *n*-pentylazomethane, bp 112° (645 Torr); the vapor pressure at 20° was 15 Torr.

PAM was characterized by its uv, nmr, and mass spectra: uv_{max} (vapor) 3545 Å (ϵ 7.5 l. mol^{-1} cm^{-1}); nmr δ 3.70 ppm for hydrogen atoms bonded to carbon adjacent to nitrogen and $\cong$ 1.2 and 0.9 ppm for methylene and methyl protons, respectively; mass spectrum (70 eV), *m/e* 114 (parent ion), 99 (weak, $C_5H_{11}N_2^+$), 85 (weak, $C_3H_6N_2CH_3^+$), 71 ($C_5H_{11}^+$), 57 ($C_4H_9^+$), 55 ($C_2H_3N_2^+$), 43 ($C_3H_7^+$), 43 ($CH_3N_2^+$), 41 ($C_3H_5^+$), 39 ($C_3H_3^+$), 29 ($C_2H_5^+$), 28 (N_2^+), and 27 ($C_2H_3^+$).

n-Pentylazomethane was stored in the vapor phase in a blackened bulb. It is stable in the dark even at 150°. Absolutely no decomposition was observed after 1 hr at that temperature. All gas handling was performed with a conventional vacuum system. The reaction vessel (9.76 cm^3) was constructed of Pyrex and was fitted with a threaded glass angle valve with a Teflon stem. Radiation from a Hanovia No. 673 A 550-W Hg arc lamp was used. The amount of pentylazomethane consumed in a run was usually between 1 and 4%. A silicone oil bath was used for temperature control.

In experiments with unfiltered radiation, the Pyrex wall of the reactor served to cut off wavelengths shorter than 3000 Å. In experiments with filtered radiation, two glass filters, Corning No. 760 and 0-52, were used together.

The entire reaction–product mixture was analyzed by gas–solid chromatography using a 2-m alumina column (60–80 mesh) and a flame ionization detector. Temperature programming from 50 to 240° was required. After 240° was reached, 30 min was required for *n*-decane elution. The alumina column was conditioned at 240° for 1–2 hr before each analysis. The azoalkane appeared to be irreversibly adsorbed on the column. Authentic samples were used for identification of the products (by comparison of retention temperatures) and for calibration. Most of the hydrocarbons needed were readily available; 4-methylnonane was purchased from Chemical Samples Co.

To avoid loss of products from absorption into stopcock grease, metal valves were employed on the gc sample inlet system. Because N_2 cannot be detected by flame ionization, it was measured by a separate procedure. After the products had been transferred under vacuum into the gc sample loop, the pressure of noncondensable gas at −196° was measured with a thermocouple gauge. This was mostly N_2 with some CH_4. This procedure was only semiquantitative; however, it did show that the material balance $(^1/_2\Sigma R)/N_2$ was ~1.0 at 25° and decreased to 0.75 at 160°. Methane was not analyzed quantitatively.

In order to test for a contribution from heterogeneous effects, two runs at 300 and 370°K were carried out in a 14-cm^3 reactor packed with glass wool. It was difficult to quantitatively remove high molecular weight products, particularly *n*-decane, from the reactor. However, the chromatogram up to hexane was identical with those runs in which no glass wool was added. Therefore, surface contributions to isomerization and decomposition were negligible.

Results and Discussion

Photochemical Activation of *n*-Pentyl Radicals. Recent studies of the photolysis of cyclic azoalkanes and ketones have demonstrated that the hydrocarbon fragments produced in the primary decomposition step can contain enough of the photolysis energy to cause them to undergo subsequent unimolecular reactions.[10] In this paper, evidence of photochemical activation in *n*-azoalkanes is presented. The maximum possible energy, E_T, available for distribution in the fragments is[11]

$$E_T = -\Delta H_R + h\nu + E^{vib}{}_{thermal} \qquad (I)$$

where ΔH_R is the enthalpy change for the reaction and $E^{vib}{}_{thermal}$ is the thermal energy in the vibrational motions of PAM. ΔH_R was assumed to be given by the value calculated for the decomposition of azomethane,[12] 22 kcal mol^{-1}. From this we calculate $\Delta H_f(PAM)$ = 23 kcal mol^{-1}.

When using unfiltered light from the Hg lamp, the superposition of the frequency distribution and the gas-phase absorption spectrum of PAM show that the most probable wavelength adsorbed is 355 mμ with a large spread from 320 to 400 mμ. This corresponds to an average photon energy of ~81 kcal mol^{-1}. When using the combination of filters described in the Experimental Section, the most probable wavelength absorbed is about 370 mμ, with a much smaller spread than in the unfiltered case, *i.e.*, 360–380 mμ. The average energy of the absorbed radiation is about 77 kcal $einstein^{-1}$. At 25° the vibrational energy of PAM is 5.3 kcal mol^{-1}. This gives E_T = 64 and 60 kcal mol^{-1} for the experiments using unfiltered and filtered light, respectively, to be distributed among the degrees of freedom of the nitrogen molecule, the methyl radical, and the *n*-pentyl radical. Since the thresholds for *n*-pentyl isomerization and decomposition are 19 and 29.6 kcal mol^{-1}, respectively,[6] both of these reactions would be possible. At 25° the principle products were ethane, *n*-pentane, pentene, *n*-hexane, and *n*-decane. Small amounts of ethylene, propylene, propane, *n*-butane, 2-methylpentane, *n*-heptane, and *n*-octane were present. The relative amounts of these latter products increased when the pressure was decreased. In the following mechanism, reactions 1–16 are considered sufficient to explain the products from experiments carried out at 25°. The asterisk indicates only the possibility of photochemically activated *n*-pentyl radicals (to an energy of at least 19 kcal mol^{-1}). Most of the *n*-C_5H_{11} radicals will not receive this much energy.

$$n\text{-}C_5H_{11}N_2CH_3 \longrightarrow n\text{-}C_5H_{11}^* + CH_3 + N_2 \qquad (1)$$

$$2CH_3 \longrightarrow C_2H_6 \qquad (2)$$

$$n\text{-}C_5H_{11}^* \xrightarrow{\omega} n\text{-}C_5H_{11}\ (S) \qquad (3)$$

$$n\text{-}C_5H_{11}^* \xrightarrow{k_a} sec\text{-}C_5H_{11}^*\ (I) \qquad (4)$$

$$n\text{-}C_5H_{11}^* \xrightarrow{k_a'} C_3H_7 + C_2H_4\ (D) \qquad (5)$$

$$2n\text{-}C_5H_{11} \longrightarrow n\text{-}C_{10}H_{22} \qquad (6)$$

$$2n\text{-}C_5H_{11} \longrightarrow n\text{-}C_5H_{12} + 1\text{-}C_5H_{10} \qquad (7)$$

$$CH_3 + n\text{-}C_5H_{11} \longrightarrow n\text{-}C_6H_{14} \qquad (8)$$

$$CH_3 + n\text{-}C_5H_{11} \longrightarrow CH_4 + 1\text{-}C_5H_{10} \qquad (9)$$

$$sec\text{-}C_5H_{11}^* \xrightarrow{\omega} sec\text{-}C_5H_{11}\ (Ss) \qquad (10)$$

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

(10) (a) R. J. Campbell, E. W. Schlag, and B. W. Ristow, *J. Amer. Chem. Soc.*, **89**, 5098 (1967); (b) F. H. Dorer, *J. Phys. Chem.*, **73**, 3109 (1969); (c) P. Cadman, H. M. Mennier, and A. F. Trotman-Dickenson, *J. Amer. Chem. Soc.*, **91**, 7640 (1969).

(11) R. J. Campbell and E. W. Schlag, *ibid.*, **89**, 5103 (1967).

(12) M. Page, H. O. Pritchard, and A. F. Trotman-Dickenson, *J. Chem. Soc.*, 3878 (1953).

$$sec\text{-}C_5H_{11} \xrightarrow{k_a''} C_2H_5 + C_3H_6\ (Ds) \tag{11}$$

$$sec\text{-}C_5H_{11} + n\text{-}C_5H_{11} \longrightarrow C_{10}H_{22}\ (4MN) \tag{12}$$

$$sec\text{-}C_5H_{11} + n\text{-}C_5H_{11} \longrightarrow n\text{-}C_5H_{12} + 1\text{-}C_5H_{10} \tag{13}$$

$$sec\text{-}C_5H_{11} + n\text{-}C_5H_{11} \longrightarrow 1\text{- or }2\text{-}C_5H_{10} + n\text{-}C_5H_{12} \tag{14}$$

$$sec\text{-}C_5H_{11} + CH_3 \longrightarrow C_6H_{14}\ (2MP) \tag{15}$$

$$sec\text{-}C_5H_{11} + CH_3 \longrightarrow 1\text{-}C_5H_{10} + CH_4 \tag{16}$$

Evidence of photochemically activated *n*-pentyl radicals with at least 19 kcal mol^{-1} can be found by measuring the ratio of stabilized isomerized radical (*sec*-pentyl) products to stabilized parent radical (*n*-pentyl) products *vs.* the pressure. According to the photochemical activation mechanism, *sec*-pentyl products should increase as the pressure or collision frequency is lowered. The expression for isomerization products divided by stabilization products, I/S, is

$$I/S = R(sec\text{-pentyl products})/R(n\text{-pentyl products})$$

which becomes equal to

$$\frac{I}{S} = \frac{1.16R(\text{2MP}) + 1.41R(\text{4MN}) + R(C_3H_6)}{R(n\text{-}C_6H_{14}) + 2.3R(n\text{-}C_{10}H_{22}) + R(n\text{-}C_5H_{12})} \tag{II}$$

The constants 1.16 and 1.41 take into account disproportionation products, and are equal to $(k_{15} + k_{16})/k_{15}$ and $(k_{12} + k_{13} + k_{14})/k_{12}$, respectively. The constant 2.3 is equal to $2(k_6 + k_7)/k_6$.

A plot of *n*-pentyl decomposition products divided by stabilized *n*-pentyl products *vs.* pressure provides evidence for photochemical activation to the 29.6-kcal mol^{-1} energy region. The expression for decomposition products is $D = R(C_2H_4) \simeq R(n\text{-}C_4H_{10}) + R(n\text{-}C_8H_{18})$.

Figure 1 shows the quantities I/S and D/S *vs.* $1/P$, using unfiltered (Pyrex cutoff) and filtered (0.52 and 7–60) light. The variation in I/S and D/S with pressure and with wavelength is consistent with the initial formation of some activated *n*-pentyl radicals which can either be deactivated by collision or react by isomerization or decomposition. Also consistent with the activation mechanism were the experiments in which CO_2 was added. They showed enhanced ratios of I/S and D/S due to the relative inefficiency of CO_2 in the deactivation of excited *n*-pentyl radicals.

It is possible to obtain quantitative information on the distribution function of formed *n*-pentyl radicals because the amounts of the isomerization and decomposition events associated with each threshold energy are indicative of the energy level populations of the activated species. The leveling off of I/S and D/S at low pressure occurs when all *n*-pentyl radicals with enough energy react, and none is stabilized. From experiments with filtered light, we estimate that ~4% of the *n*-pentyl radicals are formed with internal energies above 19 kcal mol^{-1} and ~0.2% have at least 29.6 kcal mol^{-1}. These results show the broad range of internal energies of the *n*-pentyl fragment.

The evidence for photochemical activation in this system suggests an answer to the anomalous results of Grotewold and Kerr concerning the photolysis of azo-*n*-propane.[13] When using a filter which absorbed wavelengths shorter than 3000 Å, "normal" products were observed. When using a "full-Hg-arc," which would have considerable intensity at 2537 Å, numerous hydrocarbon products were observed. An explanation is that the extinction coefficient is larger at 2537 than at 3550 Å, and the energy per einstein is 112 kcal mol^{-1}. Thus, the *n*-propyl radicals could contain considerable amounts of energy, up to ~90 kcal mol^{-1}. The threshold energy for $n\text{-}C_3H_7 \rightarrow C_2H_4 + CH_3$ is only 31 kcal mol^{-1}. We have photolyzed azo-*n*-propane with the unfiltered and filtered radiation described in this paper, and at a pressure of 0.4 Torr find very small traces of ethylene and butane.

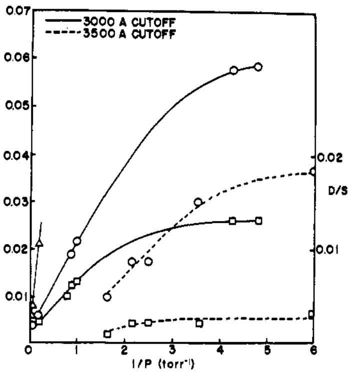

Figure 1. Plot of the functions I/S and D/S *vs.* 1/pressure: ○, I/S; □, D/S; △, I/S; CO_2 added (CO_2:PAM > 20:1).

Calvert and Pitts,[14] in reference to the photolysis of azoalkanes with 3660-Å light, state "there is little evidence of non-thermalized radicals . . . at ordinary pressures." Here we present direct evidence of the formation of excited radicals.

The Ratio of Disproportionation to Combination for the *n*-Pentyl Radical. The ratio k_7/k_6 can be estimated from the runs at 25°. This ratio cannot be obtained exactly because the disproportionation products, *n*-pentane and 1-pentene, are both formed by reactions that compete with *n*-pentyl disproportionation. *n*-Pentane is formed by H-atom abstraction by *n*-pentyl, and 1-pentene is produced by methyl–pentyl disproportionation. If H-atom abstraction is very slow, then R(1-pentene) will be greater than R(*n*-pentane), as it is in all of the runs at 25° with unfiltered light, as shown in Table I.

The lower limit to the *n*-pentyl–methyl disproportionation to combination ratio can be obtained from the expression

$$\frac{k_9}{k_8} \geqslant \frac{R(C_5H_{10}) - R(C_5H_{12})}{R(n\text{-}C_6H_{14})} \tag{III}$$

From the wide range of values for k_9/k_8 in Table I, it is evident that some abstraction is occurring. Taking only the three highest values, $k_9/k_8 \geqslant 0.033$. This is the first time that this value has been reported. It agrees with Δ(Me, Et) = 0.036[15] and Δ(Me, *n*-Bu) = 0.030,[16] but it differs significantly from Δ(Me, *n*-Pr) = 0.058.[15] However, other values reported for Δ(Me, *n*-Pr) are 0.032[17] and 0.033.[18]

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(13) J. Grotewold and J. A. Kerr, *J. Chem. Soc.*, 4337 (1963).

(14) J. G. Calvert and J. N. Pitts, Jr., "Photochemistry," Wiley, New York, N. Y., 1966, p 462.

(15) J. O. Terry and J. H. Futrell, *Can. J. Chem.*, 45, 2327 (1967), and references therein.

(16) K. W. Watkins, unpublished results.

(17) K. W. Watkins and D. A. Pavlica, presented at the Midwest Regional Meeting of the American Chemical Society, Kansas City, Mo., 1969, No. 602.

(18) J. Grotewold and J. A. Kerr, *J. Chem. Soc.*, 4324 (1963).

Table I. Product Ratios at 25°

P, Torr	ϕ^2	n-$C_{10}H_{22}$/ C_2H_6	C_5H_{12}/ n-$C_{10}H_{22}$	C_5H_{10}/ n-$C_{10}H_{22}$	($C_5H_{10} - C_5H_{12}$)/ n-C_6H_{14}	(C_5H_{10} − $0.033C_6H_{14}$)/ n-$C_{10}H_{22}$
11	3.43	0.69	0.18	0.21	0.013	0.14
12	3.91	0.64	0.23	0.25	0.009	0.17
5.7	3.81	0.68	0.18	0.22	0.014	0.14
1.1	4.05	0.58	0.20	0.25	0.025	0.16
13.	3.76	0.82	0.19	0.19	0.000	0.12
1.0	4.26	0.70	0.18	0.23	0.021	0.15
29.7[a]	3.91	0.72	0.16	0.20	0.018	0.12
16.2[a]	3.64	0.76	0.15	0.19	0.049	0.12

[a] CO_2 added.

In the presence of small amounts of H-atom abstraction by n-pentyl, an upper limit to the disproportionation to combination ratio for n-pentyl radicals can be estimated from the expression

$$\frac{k_7}{k_6} \leqslant \frac{R(n\text{-}C_5H_{12})}{R(n\text{-}C_{10}H_{22})} \qquad \text{(IV)}$$

The average from the runs in Table I gives $k_7/k_6 < 0.18$.

A more exact value can be obtained from the expression

$$\frac{k_7}{k_6} = \frac{R(C_5H_{10}) - 0.033R(n\text{-}C_6H_{14})}{R(n\text{-}C_{10}H_{22})} \qquad \text{(V)}$$

The average of all the runs in Table I is $k_7/k_6 = 0.14$. This should be a more accurate estimate of k_7/k_6 than (IV) because it is less affected by H-atom abstraction. This result compares with the recent value for Δ(n-Pe, n-Pe) of 0.15[6] and ~0.2 reported by Wijnen. Observed ratios of disproportionation to combination for the n-alkyl radicals are summarized in Table II.

Table II. Disproportionation to Combination Ratios for n-Alkyl Radicals

Radical	k_d/k_c	Temp, °C	Ref
C_2H_5	0.12	100–250	*a*
	0.130	115–150	13
	0.134	25	15
n-C_3H_7	0.14	18–150	13
	0.15	25–150	8a
	0.154	25	15
n-C_4H_9	0.14	80	8b
	0.12	70–132	*b*
n-C_5H_{11}	~0.2	63	2
	0.15	57	6
	0.14	25	This work

[a] R. K. Brinton and E. W. R. Steacie, *Can. J. Chem.*, **33**, 1840 (1955). [b] Y. Inel, *J. Phys. Chem.*, **74**, 2581 (1970).

Another ratio of interest is the cross-combination ratio ϕ(Me, n-Pe) $= R(n\text{-}C_6H_{14})/[R(C_2H_6)R(n\text{-}C_{10}H_{22})]^{1/2} = k_8/(k_2k_6)^{1/2}$. The average value from the 25° runs is $\phi = 1.96$. Wijnen reported $\phi = 1.6$. Values of ϕ for alkyl radicals fall remarkably near 2.0.[19] The results reported here for n-pentyl show no apparent deviation from the behavior of other alkyl radicals.

Isomerization of the n-Pentyl Radical. In order to study the thermal isomerization of n-pentyl radicals with a minimum of complication due to photochemical activation of n-pentyl, the experiments were carried out using filtered light, and at PAM pressures of 16–30 Torr.

The thermal isomerization was studied at 120 and 160°. The products 2-methylpentane and 4-methylnonane must originate from the combination of *sec*-pentyl radicals with methyl and n-pentyl, respectively. A new product, one which was not present at 25°, appeared in the thermal runs. This was identified as 4,5-dimethyloctane, which would result from the combination of two *sec*-pentyl radicals. The additional reactions occurring in the experiments at elevated temperatures are reactions 17–21.

$$n\text{-}C_5H_{11} \longrightarrow sec\text{-}C_5H_{11} \qquad (17)$$

$$2sec\text{-}C_5H_{11} \longrightarrow C_{10}H_{22}\ (4,5\text{-DMO}) \qquad (18)$$

$$2sec\text{-}C_5H_{11} \longrightarrow 1\text{- or }2\text{-}C_5H_{10} + n\text{-}C_5H_{12} \qquad (19)$$

$$n\text{-}C_5H_{11} + n\text{-}C_5H_{11}N_2CH_3 \longrightarrow n\text{-}C_5H_{12} + C_5H_{10}N_2CH_3 \qquad (20)$$

$$CH_3 + n\text{-}C_5H_{11}N_2CH_3 \longrightarrow CH_4 + C_5H_{10}N_2CH_3 \qquad (21)$$

The rate equation which can be derived from the reaction scheme is

$$k_{17}/k_6^{1/2} = R(sec\text{-}C_5H_{11})/R^{1/2}(n\text{-}C_{10}H_{22}) \qquad \text{(VI)}$$

where $R(sec\text{-}C_5H_{11}) = [1 + (k_{16}/k_{15})]R(2\text{-MP}) + [1 + (k_{13}/k_{12}) + (k_{14}/k_{12})]R(4\text{-MN}) + 2[1 + (k_{19}/k_{18})]R(4,5\text{-DMO})$. It was assumed that all *sec*-pentyl radicals result from the thermal unimolecular isomerization of n-pentyl radicals.

In the expression for R(*sec*-pentyl), each combination product is multiplied by 1 plus the disproportionation to combination ratio for the radicals involved. Unfortunately, none of the required ratios is known from experiment. However, they can be reasonably estimated. The ratio $k_{16}k_{15}$ was estimated to be the same as the known cross disproportionation to combination ratio for methyl and isopropyl radicals, Δ(Me, i-Pr) = 0.163.[15] The ratio $(k_{13} + k_{14})/k_{12}$ was taken from Δ(n-Pr, i-Pr) = 0.407.[15] The ratio k_{19}/k_{18} was assumed to be equal to Δ(*sec*-butyl, *sec*-butyl). There is considerable disagreement in the literature on this value. The most reliable values are 0.94[20] and 1.2.[21] For simplicity, k_{19}/k_{18} was taken to be 1.0. The rate of formation of 4,5-DMO must also be multiplied by 2, because each molecule results from two *sec*-pentyl radicals. Therefore, $R(sec\text{-pentyl}) = 1.16R(2\text{-MP}) + 1.41R(4\text{-MN}) + 4.0R(4,5\text{-DMO})$.

Values of the ratio $k_{17}/k_6^{1/2}$ are listed in Table III. A plot of log $k_{17}/k_6^{1/2}$ *vs.* $1/T$ is shown in Figure 2. A

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(19) S. W. Benson and W. B. DeMore, *Annu. Rev. Phys. Chem.*, **16**, 397 (1965).

(20) B. S. Rabinovitch and R. W. Diesen, *J. Chem. Phys.*, **30**, 735 (1959).

(21) M. Migoshi and R. K. Brinton, *ibid.*, **36**, 3019 (1962).

Table III. Relative Rate Constants and Corresponding Arrhenius Parameters

T, °K	$k_{17}/k_6^{1/2} \times 10^7$ [a]	$k_{20}/k_6^{1/2}$ [b]
391.7	2.29	3.90
392.6	2.70	3.24
393.2	2.86	3.63
393.5	2.81	3.8
394.0	2.74	3.88
432.2	17.8	6.31
433.2	16.0	9.67
433.2	17.1	8.84
433.4	15.3	9.24
435.7	16.2	10.4
	$\log A_{17}/A_6^{1/2} = 1.84$	$\log A_{20}/A_6^{1/2} = 4.94$
	$E_{17} - {}^1/_2E_6 = 15.1$ [c]	$E_{20} - {}^1/_2E_6 = 7.8$

[a] $cm^{-3/2}$ $mol^{1/2}$ $sec^{-1/2}$. [b] $cm^{3/2}$ $mol^{-1/2}$ $sec^{-1/2}$. [c] kcal/mol.

least-squares treatment of all runs between 392 and 435°K gives the activation energy difference $E_{17} - {}^1/_2E_6 = 15.1$ kcal mol^{-1}, and the A factor ratio, log $(A_{17}/A_6^{1/2}) = 1.84$. Assuming that $E = 0$ gives the activation energy $E_{17} = 15.1$ kcal mol^{-1}. Taking $A_3 = 2.3 \times 10^{13}$ cm mol^{-1} sec^{-1}, which is the association constant for methyl radicals, gives $A_{17} = 3.3 \times 10^8$ sec^{-1}. Thus, the rate constant is $k_{17} = 3.3 \times 10^8 \exp(-15.1 \times 10^3/RT)$ sec^{-1}.

The unusually low A factor is of special interest. From the presence of ethylene and propylene in the runs at elevated temperatures, it is evident that some photochemically activated *n*-pentyl radicals are still being generated in the experiments with filtered light. The thermal contribution $E^{\text{vib}}_{\text{thermal}}$ to eq I increases from 5.3 to 9.0 kcal mol^{-1} at 120°; thus, photochemical activation may not be negligible in the thermal runs. The contribution of (I) to R(*sec*-pentyl) can be roughly estimated. The ratio I/D_s, where $D_s = R(C_3H_6)$, gives the ratio of stabilized *sec*-pentyl radicals to decomposed *sec*-pentyl radicals. The five runs at 25° with filtered light give an average I/D_s of 8.2. If the ratio I/D_s is the same at 120°, then I is given by $I = 8.2R(C_3H_6)$. This approach shows that I is about 15% of R(*sec*-pentyl). A significant error due to photochemical activation would cause the A factor and the activation energy to be lower than the real values.

The activation energy found here, 15.1 kcal mol^{-1}, is substantially higher than a previously reported value[4] of 10.8 kcal mol^{-1}. The higher value is in line with a recent suggestion which indicated that the value of 10.8 kcal mol^{-1} should be lower than the true value.[6] The activation energy of 15.1 kcal mol^{-1} is in good agreement with the threshold energies, E_0, for 1,4-H-atom migration used in recent chemical activation studies.[6,7] The activation energy can be converted to E_0 by using the proper equation[22] and a frequency model of the activated complex and the *n*-pentyl radical. Using complex frequencies assumed by Watkins and Lawson, $E = 15.1$ kcal mol^{-1} is consistent with $E_0 = 16.3$ kcal mol^{-1}. They found that an E_0 of 19 kcal mol^{-1} gave the best agreement between their experimental and theoretical rate constants. Rabinovitch[7] found that an E_0 of about 15 kcal mol^{-1} was needed to get a fit of experimental and theoretical rate constants for a 5_{ss} isomerization.

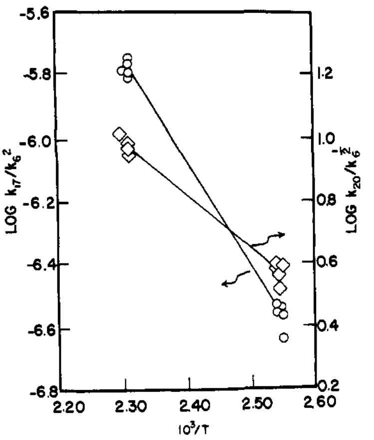

Figure 2. Arrhenius plots of functions VI and VIII from which estimates of $k_{17}/k_6^{1/2}$ and $k_{20}/k_6^{1/2}$ were derived.

Hydrogen-Atom Abstraction by *n*-Pentyl Radicals. *n*-Pentane is formed principally in reactions 20, 7, 13, 14, and 19. The rate constant ratio $k_{20}/k_6^{1/2}$ can be calculated from expression VII. Values of $k_{20}/k_6^{1/2}$

$$\frac{k_{20}}{k_6^{1/2}} = \frac{R(n\text{-}C_5H_{12}) - 0.14R(n\text{-}C_{10}H_{22}) - 0.41R(\text{4-MN}) - 1.0R(\text{DMO})}{[\text{PAM}]_0 R^{1/2}(n\text{-}C_{10}H_{22})} \qquad \text{(VII)}$$

are listed in Table III. Figure 2 shows an Arrhenius plot of log k_{20}/k_6 *vs.* $1/T$. The rate constant determined from a least-squares calculation was $k_{20} = 4.2 \times 10^{11} \exp(-7.8 \times 10^3/RT)$ mol^{-1} cm^3 sec^{-1}, assuming k_6 as in the previous section. This is the first determination of this rate constant. The values of E_{20} and A_{20} are in agreement with existing data for other primary alkyl radicals.[8c]

Acknowledgment. I wish to thank Mr. D. A. Pavlica for preparing the *n*-pentylazomethane.

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[22] S. Glasstone, K. J. Laidler, and H. Eyring, "The Theory of Rate Processes," McGraw-Hill, New York, N. Y., p 195.