Disproportionation and Recombination Reactions of Methyl and n-Pentyl Radicals[1]
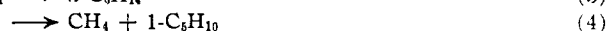
BY M. H. J. WIJNEN

Methyl and n-pentyl radicals were produced by photolysis of 2-heptanone. The primary process in the photolysis of this compound may be given by

$$CH_3CO(CH_2)_4CH_3 + h\nu \longrightarrow CH_3COCH_3 + C_4H_8 \qquad (1)$$
$$\longrightarrow CH_3CO + (CH_2)_4CH_3 \qquad (1b)$$
$$\longrightarrow CH_3 + CH_3(CH_2)_4CO \qquad (1c)$$
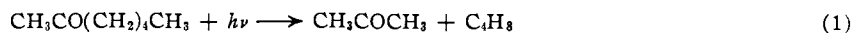
These reactions of methyl and n-pentyl radicals have been investigated

$$2CH_3 \longrightarrow C_2H_6 \qquad (2)$$
$$CH_3 + n\text{-}C_5H_{11} \longrightarrow n\text{-}C_6H_{14} \qquad (3)$$
$$\longrightarrow CH_4 + 1\text{-}C_5H_{10} \qquad (4)$$
$$2n\text{-}C_5H_{11} \longrightarrow n\text{-}C_{10}H_{22} \qquad (5)$$
$$\longrightarrow n\text{-}C_5H_{12} + 1\text{-}C_5H_{10} \qquad (6)$$

Data at 63 and at 91° indicate $k_3/(k_2^{1/2}k_5^{1/2}) = 1.6 \pm 0.1$. Approximate values of 0.1 and 0.2 are suggested for k_4/k_3 and k_6/k_5, respectively. These figures are compared with similar ratios of rate constants for other alkyl radicals.
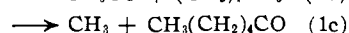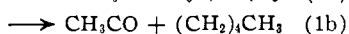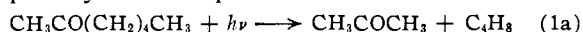
Introduction

Recently information has become available on the reactions of n-butyl,[2a] s-butyl,[2b] t-butyl[2b] and isobutyl[2b] radicals. It seemed interesting to extend this information to n-pentyl radicals. We have, therefore, photolyzed 2-heptanone, hoping to obtain data not only on the disproportionation and recombination of n-pentyl radicals but at the same time also on disproportionation and recombination reactions of methyl and n-pentyl radicals.

Experimental

The experimental technique is essentially the same as described elsewhere.[3] The amount of conversion was about 2% of the starting material. The reaction cell was separated from the high vacuum system by a Hoke valve. The reaction cell, Hoke valve and tubing leading from cell to valve were heated to prevent condensation of 2-heptanone outside the cell. The reaction products were: carbon monoxide, methane, ethane, ethylene, butane, butene, n-pentane, 1-pentene, n-hexane, 2-methylpentane, acetone and n-decane. Analysis was carried out by gas chromatography. Table I gives the observed product distribution under various experimental conditions.

Results

Primary Steps.—The following primary steps are proposed to explain the reaction products of the photolysis of 2-heptanone
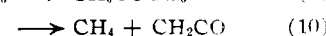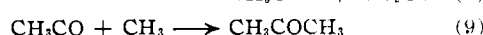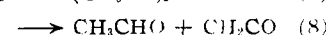
$$CH_3CO(CH_2)_4CH_3 + h\nu \longrightarrow CH_3COCH_3 + C_4H_8 \quad (1a)$$
$$\longrightarrow CH_3CO + (CH_2)_4CH_3 \quad (1b)$$
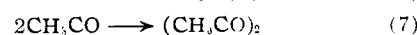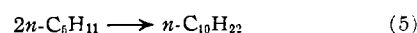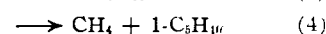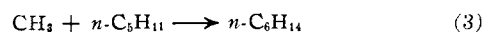$$\longrightarrow CH_3 + CH_3(CH_2)_4CO \quad (1c)$$

Step 1a is the Norrish "Type II" primary process observed in the photolysis of aldehydes and ketones having a straight chain of at least three carbon atoms attached to the carbonyl group. Within experimental error equal amounts of acetone and butene are formed (Table I). This proves the occurrence of this step in the photolysis of 2-heptanone. Steps 1b and 1c are the free radical producing steps. It is well known from the photol-

ysis of acetone and other CH_3CO producing compounds that the CH_3CO radical survives long enough at low temperatures to take part in radical-radical reactions. Masson and co-workers[4,5] observed that $CH_3CH_2CH_2CO$ and $(CH_3)_2CHCO$ radicals are very unstable and that these radicals even at 50° decompose quantitatively into CO and C_3H_7 radicals. Similarly $CH_3(CH_2)_4CO$ radicals may be expected to decompose immediately into CO and n-pentyl radicals.

Above 140° all CH_3CO radicals decompose thermally into CH_3 and CO. At these temperatures it is thus possible to calculate the relative importance of step 1a to the radicals producing steps 1b and 1c, from the ratio $R_{C_4H_8}/R_{CO}$ or $R_{CH_3COCH_3}/R_{CO}$. Our results in Table I give a value of 3.3 ± 0.2 for this ratio at 149 and at 200°. This indicates that about 77% of the total primary process leads to butene and acetone via the molecular rearrangement process step 1a. At 63° the ratios $R_{C_4H_8}/R_{CO}$ and $R_{CH_3COCH_3}/R_{CO}$ vary with initial pressure of 2-heptanone and with absorbed light intensity as expected from the increased stability of the CH_3CO radical at this temperature.

Disproportionation and Recombination Reactions.—From the discussion of the primary process it is clear that at temperatures below 110° the following radicals are present in our system: CH_3, n-C_5H_{11} and CH_3CO. The following disproportionation and recombination reactions should therefore be considered.

$$2CH_3 \longrightarrow C_2H_6 \qquad (2)$$
$$CH_3 + n\text{-}C_5H_{11} \longrightarrow n\text{-}C_6H_{14} \qquad (3)$$
$$\longrightarrow CH_4 + 1\text{-}C_5H_{10} \qquad (4)$$
$$2n\text{-}C_5H_{11} \longrightarrow n\text{-}C_{10}H_{22} \qquad (5)$$
$$\longrightarrow 1\text{-}C_5H_{10} + n\text{-}C_5H_{12} \qquad (6)$$
$$2CH_3CO \longrightarrow (CH_3CO)_2 \qquad (7)$$
$$\longrightarrow CH_3CHO + CH_2CO \qquad (8)$$
$$CH_3CO + CH_3 \longrightarrow CH_3COCH_3 \qquad (9)$$
$$\longrightarrow CH_4 + CH_2CO \qquad (10)$$

(1) This investigation was supported, in part, by the U. S. Atomic Energy Commission.

(2) (a) J. A. Kerr and A. F. Trotman-Dickenson, *J. Chem. Soc.*, 1602 (1960); (b) J. W. Kraus and J. G. Calvert, *J. Am. Chem. Soc.*, **79**, 5921 (1957).

(3) K. O. Kutschke, M. H. J. Wijnen and E. W. R. Steacie, *ibid.*, **74**, 711 (1952).
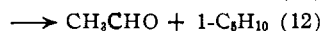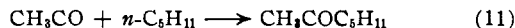
(4) C. R. Masson, *ibid.*, **74**, 4731 (1952).

(5) S. G. Whiteway and C. R. Masson, *ibid.*, **77**, 1508 (1955).

TABLE I
PHOTOLYSIS OF 2-HEPTANONE[a]

Run No.	11	12	13	14	15	16	17	18	19	20
$[H]_0$, molec./cc. $\times 10^{-17}$	4.34	8.68	6.51	6.51	6.51	6.51	6.51	6.51	6.51	6.51
Int. relat. %	100	100	100	30	9	9	100	100	9	100
Temp., °C.	63	63	63	63	63	63	63	149	149	200
Rates of products in molec./(sec. cc.) $\times 10^{-12}$										
R_{CO}	1.03	1.78	1.52	0.58	0.24	0.24	1.52	3.02	0.31	2.94
R_{CH_4}	0.23	0.56	0.51	0.33	0.19	0.18	0.65	2.33	0.29	2.80
$R_{C_2H_6}$	0.23	0.33	0.26	0.08	0.02	0.02	0.23	0.23	0.01	0.16
$R_{C_3H_4}$	...	...	...	...	...	...	...	...	...	.06
$R_{C_3H_8}$	...	...	...	...	...	...	...	...	...	.10
$R_{C_3H_6}$	...	...	...	...	...	...	...	...	...	.27
$R_{C_4H_{10}}$	...	...	...	...	...	...	...	...	...	.02
$R_{C_4H_8}$	8.33	12.99	10.95	3.57	1.28	1.19	10.34	10.55	1.04	9.13
$R_{CH_3COCH_3}$	8.12	13.65	11.60	3.72	1.28	1.23	10.23	10.79	1.11	9.75
$R_{C_6H_{13}}$	0.21	0.41	0.36	0.21	0.11	0.09	0.36	0.89	0.13	1.01
$R_{C_6H_{10}}$	.06	.12	.08	.02	.005	.005	.09	.23	.02	0.40
$R_{(CH_3)_2CH(CH_2)_3CH_3}$	...	...	...	...	...	...	...	.07	.01	.09
$R_{CH_3(CH_2)_4CH_3}$	.35	.50	.35	.10	.02	.02	.32	.18	.01	.02
$R_{C_{10}H_{22}}$ calcd.	.21	.30	.46	.05	.01	.01	.18	.06	...	...
$R_{C_6H_{10}}/R_{C_{10}H_{22}}$	.3	.4	.2	.4	.5	.5	.5	3.8	...	...
$R_{C_6H_{10}}/(2R_{C_6H_{14}} + 4R_{C_{10}H_{22}})$	.04	.05	.035	.04	.055	.055	.06	...	...	...

[a] Open spaces indicate that under the given conditions this compound was not formed or formed in too small amounts to allow its determination by gas chromatography.

$$CH_3CO + n\text{-}C_5H_{11} \longrightarrow CH_3COC_5H_{11} \quad (11)$$
$$\longrightarrow CH_3CHO + 1\text{-}C_5H_{10} \quad (12)$$
$$\longrightarrow CH_2CO + n\text{-}C_5H_{12} \quad (13)$$

It is obvious that in addition to the above-mentioned radical–radical reactions hydrogen abstraction reactions from 2-heptanone will also occur. We will limit our discussion, however, to products exclusively produced by disproportionation and recombination reactions. As sole modes of formation for C_2H_6, $n\text{-}C_6H_{14}$ and $n\text{-}C_{10}H_{22}$ are suggested reactions 2, 3 and 5. The following equation may then be derived

$$R_{n\text{-}C_6H_{14}}/(R_{n\text{-}C_{10}H_{22}}^{1/2} \times R_{C_2H_6}^{1/2}) = k_3/(k_2^{1/2}k_5^{1/2})$$

Experiments at 63 and at 91° (not reported in Table I) gave a constant value of 1.6 ± 0.1 for $k_3/(k_2^{1/2}k_5^{1/2})$. This value is in good agreement with similar ratios of rate constants observed for other alkyl radicals.[6] We have used this value to calculate the amounts of n-decane produced from the amounts of ethane and n-hexane for the results reported in Table I.

Limiting the discussion temporarily to the results at 63° reported in Table I, 1-pentene may be formed by reactions 4, 6 and 12. Unfortunately it is impossible to obtain an accurate estimate of the extent to which reaction 12 takes part in the formation of 1-pentene. The CH_3CO radicals undoubtedly react predominantly with CH_3 and $n\text{-}C_5H_{11}$ radicals to form CH_3COCH_3 and $C_5H_{11}COCH_3$ according to reactions 9 and 11. Since $C_5H_{11}COCH_3$ is the starting material and since acetone is produced in large quantities by primary step 1c, it is impossible to obtain estimates about the formation of these compounds via reactions 9 and 11. However, the fact that we have not observed biacetyl, acetaldehyde and ketene indicates that the concentration of CH_3CO radicals must be

small. This is easily understood if we realize that CH_3CO radicals partly decompose into CH_3 and CO. It seems thus reasonable to neglect reaction 12 as contributing in any appreciable amount to the formation of 1-pentene.

In any case a maximum value for k_6/k_5 may be obtained from the ratio $R_{1\text{-}C_5H_{10}}/R_{n\text{-}C_{10}H_{22}}$. Data at 63° reported in Table I indicate $R_{1\text{-}C_5H_{10}}/R_{n\text{-}C_{10}H_{22}} = 0.4 \pm 0.1$. The following calculation may be carried out if we accept, as has been pointed out recently,[2b,7] that the amount of disproportionation is predominantly determined by the number of hydrogen atoms available for disproportionation. In reaction 4 two hydrogen atoms and in reaction 6 four hydrogen atoms are available for disproportionation. Thus, the ratio $R_{1\text{-}C_5H_{10}}/(2R_{n\text{-}C_5H_{14}} + 4R_{n\text{-}C_{10}H_{22}})$ should be constant and should give the ratio of disproportionation over recombination per available hydrogen atom. The last row in Table I shows the results obtained at 63° and from this we obtain $k_4/k_3 \simeq 0.1$ and $k_6/k_5 \simeq 0.2$. It would have been interesting to carry these calculations out for the data at higher temperatures. Unfortunately at higher temperatures the reaction mechanism becomes complex due to the fact that sec-pentyl radicals are produced. This is clearly shown by the fact that 2-methylpentane is observed as a reaction product. This product may be explained by the reactions

$$(CH_2)_4CH_3 \longrightarrow CH_3CH(CH_2)_2CH_3$$
$$CH_3 + CH_3CH(CH_2)_2CH_3 \longrightarrow (CH_3)_2CH(CH_2)_2CH_3$$
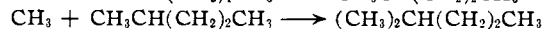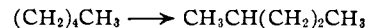
Isomerization of the n-pentyl radical to the sec-pentyl radical has been observed previously by Gordon and McNesby[8] at about 300°. Our data indicate that this reaction is already important at temperatures as low as 150°. No other data are

(6) J. A. Kerr and A. F. Trotman-Dickenson. *Chem. and Ind.* (London), 125 (1959).

(7) P. Ausloos and E. W. R. Steacie. *Can. J. Chem.*, **33**, 1062 (1955).

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

reported in the literature for k_4/k_3 and k_6/k_5. In Table II we have summarized recent data on disproportionation over recombination for normal alkyl radicals. The data reported for n-butyl radicals should be taken as maximum values since the authors assumed that all butene originated from disproportionation of n-butyl radicals. Other radicals were, however, present in their system. Butene may, therefore, be formed not only by

TABLE II

RATIOS OF DISPROPORTIONATION OVER RECOMBINATION FOR n-ALKYL RADICALS

	D/R	Author
$CH_3 + C_2H_5$	0.04	Ausloos and Steacie[a]
	.06	Heller[b]
$CH_3 + n$-C_3H_7	.05	Ausloos and Murad[c]
$CH_3 + n$-C_4H_9	?	
$CH_3 + n$-C_5H_{11}	≈0.1	This investigation
$C_2H_5 + C_2H_5$	.12	Ausloos and Steacie[a]
	.14	James and Steacie[d]
	.15	Brinton and Steacie[e]

n-$C_3H_7 + n$-C_3H_7	.15	Ausloos and Murad[c]
	.10	Blacet and Calvert[f]
	.17	Masson[g]
n-$C_4H_9 + n$-C_4H_9	0.57–1.09	Kerr and Trotman-Dickenson[h]
n-$C_5H_{11} + n$-C_5H_{11}	≈0.2	This investigation

[a] Ref. 7. [b] C. A. Heller, *J. Chem. Phys.*, **28**, 1255 (1958). [c] P. Ausloos and E. Murad, *J. Am. Chem. Soc.*, **80**, 5929 (1958). [d] D. G. L. James and E. W. R. Steacie, *Proc. Roy. Soc. (London)*, **A244**, 289 (1958). [e] R. K. Brinton and E. W. R. Steacie, *Can. J. Chem.*, **33**, 1840 (1955). [f] F. E. Blacet and J. G. Calvert, *J. Am. Chem. Soc.*, **73**, 661 (1951). [g] Ref. 4. [h] Ref. 2a.

the reaction $2n$-$C_4H_9 \rightarrow C_4H_{10} + C_4H_8$ but also by $R + n$-$C_4H_9 \rightarrow C_4H_8 + RH$. Excluding the data on n-butyl radicals Table II indicates that there is a general agreement on the relative importance of disproportionation and recombination reactions of normal alkyl radicals.

[Contribution from the Department of Chemistry, University of California, Berkeley, California]

Hydrogen Abstraction from Hydrocarbons by Methyl Radicals from the Photolysis of Methyl Iodide in Solid Nitrogen

By C. David Bass and George C. Pimentel

Methyl iodide has been photolyzed at 20°K. in solid matrix materials, N_2, Kr and Xe, containing hydrocarbons [C_2H_6 or $(CH_3)_3CH$] or deuterated hydrocarbons [CD_4, CH_3CD_3, or $(CH_3)_3CD$]. Hydrogen abstraction was studied by infrared detection of CH_4 and CH_3D. In the solid the abstraction products can be attributed to methyl radicals with an "effective temperature" in the range 1000–3000°K. Furthermore, the products obtained from photolysis of methyl iodide with ethane present as well as those from photolysis of ethyl iodide in nitrogen, indicate that about 85% of the reactions probably occur within the cage at the site of photon absorption. These studies provide information concerning the dissipation of the energy of a "hot" radical constrained within a reactive cage.

The "cage effect" hypothesis explains the characteristically low quantum yield of primary dissociation in a condensed medium.[1] The solvent molecules surrounding a site of photon absorption form a "cage"; in collisions with this environment, primary fragments dissipate excess energy before separating far enough to escape recombination. Though the qualitative features of the cage effect have been discussed by a number of workers,[2] much less is known about the quantitative aspects of this process.

Evidence concerning the cage inhibition of photolytic decompositions in matrix isolation studies has been reviewed by Pimentel.[3] It is clear that some substances, for example methyl iodide, resist photolytic decomposition even though the excitation energy which must be dissipated (per mole) may be more than one hundred times the

molar heat of fusion of the solid environment (as it is in solid argon or nitrogen). We have sought a more detailed understanding of the fate of the excitation energy through studies of the abstraction of hydrogen and deuterium from hydrocarbons by methyl radicals produced through photolysis of methyl iodide in solid nitrogen.

Experimental

The gases were mixed in a three-liter flask in a vacuum system. The bulb was painted black to prevent gas phase photolysis reactions and it contained Teflon chips for mixing. Approximately 10^3 micromoles of the hydrocarbon was admitted to the bulb and condensed at 77°K. Then 10^3 micromoles of methyl iodide was measured into a smaller calibrated flask and transferred to the larger flask at 77°K. Finally, 25×10^3 micromoles of the matrix gas was expanded into the sample flask. The concentrations, expressed in mole ratios, are approximately: M/RH = 25 and M/CH₃I = 250 (M = matrix, RH = hydrocarbon). The flask was shaken to agitate the Teflon chips and thus to ensure mixing.

The vapor pressure of CD_4 at 77°K. is about 20 mm. Therefore, when RH was CD_4, the order of introducing hydrocarbon and methyl iodide was reversed.

The low temperature cell was a duplicate of a cell designed by Van Thiel.[4] The gaseous mixture was admitted to the cell at reduced pressure by passing it through a metal needle

(1) I. Franck and E. Rabinowitch, *Trans. Faraday Soc.*, **30**, 120 (1934).

(2) See, for example, F. W. Lampe and R. M. Noyes, *J. Am. Chem. Soc.*, **76**, 2140 (1954); M. Szwarc, *J. Polymer Sci.*, **16**, 367 (1955); R. Luebbe and J. Willard, *J. Am. Chem. Soc.*, **81**, 761 (1959), and references cited therein.

(3) Chapter IV, "Radical Formation and Trapping in the Solid Phase," by G. C. Pimentel, "Formation and Trapping of Free Radicals," ed. A. Bass and H. Broida. Academic Press, Inc., New York, N. Y., 1960.

(4) M. Van Thiel, Ph.D. Thesis, University of California, Berkeley, 1958.