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}	$\approx$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}	$\approx$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.

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

(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.

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/CH_3I = 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

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

valve (Hoke) greased with Apiezon-N lubricant. When the matrix was N_2, the spray-on rate was 40 to 60 mm./hour from the three liter bulb (about 160 micromoles/min.). The matrix materials Kr and Xe required slower deposition (about 6 mm./hour) to reduce light scattering. Approximately 5×10^3 micromoles of the gas mixture was deposited in each experiment.

Infrared spectra were recorded using a Beckman IR-7 or a Perkin-Elmer Model 21 spectrophotometer, as indicated in the tables. Frequency measurements were made with the IR-7 instrument and the reproducibility was ± 2 cm.$^{-1}$. Intensity reproducibility was better than 10%. Slit widths were small compared to band widths: effective band widths were 1.3 cm.$^{-1}$ at 960 cm.$^{-1}$, 1.7 cm.$^{-1}$ at 1150–1250 cm.$^{-1}$ and 1.5 cm.$^{-1}$ at 1300 cm.$^{-1}$. (For experiments using the Perkin-Elmer 21, the effective band widths were somewhat larger but still smaller than the observed widths of the bands.)

The samples were irradiated with light from a General Electric HA-4 medium pressure mercury arc with the outer Pyrex jacket removed. The beam was focused on the sample with a fused quartz lens. Output of the lamp was at least 10^{18} quanta per hour.

Chemical Preparations.—CH_3D.—This compound, synthesized by Grignard reaction from CH_3I, contained 95% CH_3D and 5% CH_4.[5] There was a negligible amount of CH_2D_2.

$(CH_3)_3CD$.—This compound, synthesized by Grignard reaction,[6] was washed through concentrated H_2SO_4 with nitrogen gas (which removed butenes) and frozen at 77°K. The sample contained about 70% $(CH_3)_3CD$ and 30% $(CH_3)_3CH$.[5]

C_2H_6 (Phillips), CH_4 (Phillips), $(CH_3)_3CH$ (Matheson), C_2H_4 (Phillips), CD_4 (Bio-Rad Laboratories), CH_3CD_3 (Merck).—These samples were purchased, and each was stated to be 99 mole % pure.

CH_3I (Eastman Kodak, reagent).—Methyl iodide was outgassed at 77°K. three times and then once again before each experiment.

N_2 (General Dynamics Corp.).—Nitrogen gas was passed over copper filings at 500° to remove traces of O_2. The gas was passed through a trap at 77°K. and collected in a large storage flask.

Xe (Air Reduction Sales Co.).—Stated impurities (by mass spectrometric analysis) in mole % were: H_2, 0.005; N_2, 0.005; Kr, 0.005; O_2, 0.001.

Kr (Air Reduction Sales Co.).—Stated impurities (by mass spectrometric analysis) in mole per cent. were: H_2, less than 0.001; N_2, 0.005; Xe, 0.010.

Results

Absorption Coefficients of Products.—Qualitative and quantitative analyses were based on reference spectra of known samples suspended in the appropriate matrix under conditions duplicating the photolysis experiments. The sample was deposited in several measured fractions to provide a curve of growth. The spectrum was recorded for each fraction and the peak intensity was plotted vs. micromoles deposited.[7] Unfortunately, only a fraction of the sample actually is condensed in the optical path (probably more than two thirds of the sample). Though the absolute extinction coefficients are not known, the ratios of true extinction coefficients can be measured provided only that all of the compounds studied have the same accommodation coefficients. The ratios are sufficient for the purposes of a material balance. The apparent extinction coefficients are given in

(5) We are grateful to Dr. B. H. Mahan and Dr. A. Newton for mass spectral analyses of the CH_3D and $(CH_3)_3CD$ samples.

(6) We are grateful to Dr. A. C. McRowe for his preparation of $(CH_3)_3CD$.

(7) The area, rather than the peak absorption, was measured for the band of ethylene at 960 cm.$^{-1}$ because the band was found to broaden from a half-width near 5 cm.$^{-1}$ to about 20 cm.$^{-1}$ if diffusion was permitted. This change in band shape resulted in no change in the band area, within experimental uncertainty.

Table I in terms of the peak value of log I_0/I per micromole. When a range is given, deviation from Beer's law was observed. The lowest value corresponds to the limiting slope and the higher value gives the slope when 30 micromoles of sample was deposited. All quantitative interpretations discussed here are based on the actual curves of growth. In any experiment in which both CH_3D and CH_4 were produced, the absorption at 1304 cm.$^{-1}$ caused by CH_3D was estimated from the intensity of the band at 1155 cm.$^{-1}$. This small correction was subtracted and the remainder was ascribed to CH_4.

TABLE I

APPARENT ABSORPTION COEFFICIENTS OF VARIOUS SUBSTANCES SUSPENDED IN SOLID NITROGEN[a]

$T = 20°K.$, $D_0 = $ peak value of log I_0/I per micromole.

Substance	ν(cm.$^{-1}$)	D_0
CH_3I	1248	0.0098 – 0.0061
C_2H_5I	1215	.011
C_2H_4	960	.038 (0.015[b])
CH_4	1304	.0137
CH_3D	1155	.0055 ± 0.0003
	1304	.0027 ± 0.0003

[a] The curves of growth are presented in the Ph. D. thesis of C. D. Bass, University of California, Berkeley, 1961. [b] Peak absorption after warming sample to about 40°K. and recooling to 20°K.

TABLE II

PHOTOLYSIS OF CH_3I IN VARIOUS MATRICES CONTAINING C_2H_4

$$\frac{M}{CH_3I} = 210; \quad \frac{M}{C_2H_4} = 21; \quad T = 20°K.$$

Matrix	Photolysis time (min.)	CH_3I 1248 cm.$^{-1}$	CH_4 1304 cm.$^{-1}$	C_2H_4[a] 960 cm.$^{-1}$	μmoles CH_3I	$\frac{CH_4}{\Delta CH_3I}$[b]	$\frac{C_2H_4}{CH_4}$
N_2	0	0.163	...	..	17.0	..	..
	10	.117	0.058	..	11.8	0.79	..
	30	.091	.105	21	9.1	.95	0.69
	60	.076	.126	32	7.6	.95	.89
	120	.063	.151	33	6.3	1.00	.78
Kr	0	.149	...	..	15.3	..	..
	10	.116	.030	..	11.8	0.60	..
	30	.088	.059	10	8.8	.64	.59
	60	.077	.084	18	7.7	.77	.77
	120	.057	.104	30	5.7	.78	1.00
Xe	0	.117	...	..	11.8	..	..
	10	.084	.023	5	8.4	.47	0.77
	30	.068	.045	ᵉ	6.8	.64	ᵉ
	60	.053	.071	20	5.3	.77	1.00
	120	.040	.094	31	4.0	.86	1.10

[a] Integrated intensities.[7] [b] ΔCH_3I equals the decrease in micromoles of CH_3I from time = 0. [e] Not measured.

C_2H_5I in N_2.—Ethyl iodide, methane, ethane and nitrogen were mixed in the mole ratios 1:1:20:480 and condensed at 20°K. The sample, containing 27.5 micromoles of ethyl iodide (log $I_0/I = 0.302$ at 1215 cm.$^{-1}$), was photolyzed for 30 minutes and 79% of the C_2H_5I was decomposed. Ethylene was produced (16.0 micromoles) as revealed by the absorption at 960 cm.$^{-1}$ (see footnote 7). The ratio of micromoles C_2H_4 produced per micromole C_2H_5I decomposed was 0.76.

$CH_3I + C_2H_6$ in N_2, Kr, and Xe.—The results of experiments in which CH_3I was photolyzed in the

Table III

Photolysis of CH₃I in Nitrogen Containing Hydrocarbons

$T = 20°K., M/CH_3I = 220$

Expt. no.	Composition	Photolysis Time (min.)	$\log I_0/I$ CH₃I 1248 cm.⁻¹	CH₄ 1304 cm.⁻¹	CH₃D 1155 cm.⁻¹	μmoles CH₃I	$\dfrac{CH_4}{CH_3D}$	$\dfrac{CH_4 + CH_3D}{\Delta CH_3I}$ [b]
1	CD₄[a]	690	[c]	0.02	<0.005	[c]	...	...
	M/CD₄ = 25							
2	C₂H₆ + CD₄	0	0.198	...	...	21.5	...	...
	M/C₂H₆ = 45	120	.086	.140	< .005	8.7	>12	0.77
	M/CD₄ = 35	360	.076	.159	< .005	7.6	>13	.80
3'	CH₃CD₃	0	.171	...	...	18.1	...	...
	M/CH₃CD₃ = 21	10	.137	.027	.009	14.0	1.04	.78
		30	.109	.054	.016	10.9	1.17	.84
		60	.096	.067	.021	9.6	1.10	.91
3"	CH₃CD₃	0	.183	...	...	19.6	...	...
	M/CH₃CD₃ = 21	10	.155	.030	.010	16.0	1.01	.99
		30	.121	.060	.016	12.3	1.32	.89
		60	.097	.076	.021	9.7	1.27	.85
3'''	CH₃CD₃	0	.183	...	...	19.6	...	...
	M/CH₃CD₃ = 21	10	.142	.035	.010	14.5	1.21	.77
		30	.111	.061	.018	11.4	1.17	.84
		60	.096	.076	.023	9.6	1.15	.87
4'	(CH₃)₃CH	0	.231	...	...	26.1	...	...
	M/RH = 21	10	.192	.054	...	20.7	...	.71
		30	.161	.115	...	16.7	...	.86
		60	.129	.177	...	13.2	...	.96
		120	.104	.244	...	10.4	...	1.10
4"	(CH₃)₃CH	0	.220	...	...	24.6	...	...
	M/RH = 21	10	.175	.061	...	18.6	...	0.72
		30	.136	.123	...	14.0	...	0.81
		60	.120	.176	...	12.2	...	1.01
		120	.093	.233	...	9.3	...	1.08
5	(CH₃)₃CD	0	.213	...	...	23.6	...	...
	M/RD = 21	10	.151	.048	< .005	15.6	> 4	0.43
		30	.123	.094	< .005	12.5	> 8	.60
		120	.086	.164	.014	8.7	4.5	.91

[a] M/CH₃I = 295; P. E. Model 21 used in this experiment only. [b] ΔCH₃I equals the decrease in micromoles of CH₃I from time = 0. [c] Not measured.

presence of C_2H_6 in N_2, Kr and Xe matrices are shown in Table II. To decrease photometric uncertainties in these and in later measurements, each spectrum was recorded three times. After averaging, the uncertainty in each value of log I_0/I was about 0.003.

In each experiment, photolysis produced a broad absorption near 960 cm.⁻¹ and a sharper band near 1304 cm.⁻¹. The band near 1304 cm.⁻¹ is considered to arise from methane and the broad absorption is assigned to ethylene. All of these spectra were interpreted in terms of micromoles of CH_4 and C_2H_4 produced and of CH_3I decomposed using the absorption coefficients measured for nitrogen matrix. This implies additional uncertainty in the results for the Kr and Xe experiments, though the similar band widths in the three matrix materials provide some support for the procedure. (Similar experiments carried out in CO_2 matrix are not reported here since the band widths indicated the nitrogen matrix curves of growth could not be applicable.)
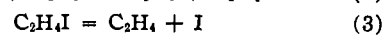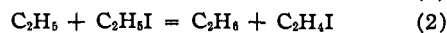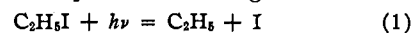
Hydrogen and Deuterium Abstraction from Hydrocarbons.—The results of other abstraction experiments are given in Table III. No CH_3D was detected either in experiment no. 1 or no. 2.

The minimum detectable amount is estimated to be about 0.9 micromole (see Table I). This absence of abstraction from CD_4 is consistent with another experiment (not reported in Table III) in which CH_3I was photolyzed in pure, solid CD_4 at 20°K.(CD_4/CH_3I = 580). Though photolysis was continued for 360 minutes, no trace of CH_3D could be detected.

In all other experiments, no. 3 to 5, significant amounts of CH_3D and/or CH_4 were produced.

Discussion

Photolysis of C_2H_5I in Solid Nitrogen.—In the photolysis of gaseous ethyl iodide, the products are approximately 50% C_2H_6 and 50% C_2H_4.[8] To account for this ratio, West and Schlessinger proposed a reaction sequence including the reactions

$$C_2H_5I + h\nu = C_2H_5 + I \qquad (1)$$
$$C_2H_5 + C_2H_5I = C_2H_6 + C_2H_4I \qquad (2)$$
$$C_2H_4I = C_2H_4 + I \qquad (3)$$
$$I + I = I_2 \qquad (4)$$

In the present work, ethylene is again a product but the ratio (moles C_2H_4)/(moles C_2H_5I decom-

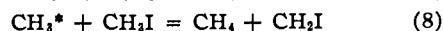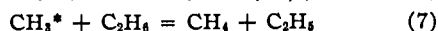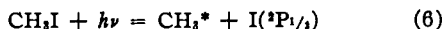(8) W. West and L. Schlessinger, J. Am. Chem. Soc., 60, 961 (1938).

posed) is 0.76 ± 0.1. This ratio exceeds the gas phase value, 0.50, presumably because of cage effect. Reaction 1 is apparently followed to a considerable extent by a reaction within the cage to produce ethylene and HI.

$$C_2H_5 + I = C_2H_4 + HI \qquad (5)$$
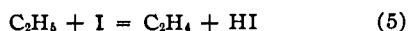
Hydrogen Abstraction from Ethane: Material Balance.—Of the hydrocarbons studied, ethane is the most convenient compound from which to detect reaction products. A quantitative material balance was sought.

Hydrogen abstraction was indicated by the growth of the band near 1304 cm.$^{-1}$, attributed to CH_4. The fraction of the photolysis which results in methane formation is given by the ratio (moles CH_4)/(moles CH_3I decomposed) $= CH_4/\Delta(CH_3I)$, as shown in Table II (column 7). In nitrogen matrix, the fraction is approximately constant and accounts for 90 ± 10% of the decomposed CH_3I. In the other matrices, Kr and Xe, there seem to be trends in the data. For short photolysis times there seems to be substantial loss of CH_3I without formation of CH_4.

Presumably the methane is produced in the successive reactions

$$CH_3I + h\nu = CH_3{}^* + I(^2P_{1/2}) \qquad (6)$$
$$CH_3{}^* + C_2H_6 = CH_4 + C_2H_5 \qquad (7)$$
$$CH_3{}^* + CH_3I = CH_4 + CH_2I \qquad (8)$$

Reaction 8 contributes a negligible amount of CH_4, as shown by experiment 1 in Table III (note the photolysis time) and other experiments in which only CH_3I was present in the N_2 matrix. This focuses attention on reaction 7 and raises the question concerning the other product, C_2H_5. A possible fate for C_2H_5 is reaction with the iodine atom produced by reaction 1, to give C_2H_5I. Yet no absorption was ever detected in the region near 1215 cm.$^{-1}$. As shown in Table I, as little as 0.5 micromole of C_2H_5I could have been detected. Absorption was observed at 960 cm.$^{-1}$ which, in absence of absorption at 1215 cm.$^{-1}$, can be assigned to ethylene. It is likely that the products of 6 and 7 react to form C_2H_4 by reaction 5 (for which $\Delta H = -28$ kcal./mole). Absorption assignable to HI (at 2180 cm.$^{-1}$) was detected but quantitative measurement was precluded by the low absorption coefficient of HI. Even if reaction 5 is accompanied by reaction 9

$$C_2H_5 + I = C_2H_5I \qquad (9)$$

secondary photolysis of C_2H_5I would prevent accumulation of C_2H_5I and would yield the same products by reactions 1 and 5.

The amount of ethylene in the nitrogen matrix experiments averaged 80 ± 10% of the amount of CH_4. For the rare gas matrices, Kr and Xe, there seems to be a trend in the ratio (moles C_2H_4)/(moles CH_4). For short photolyses, the ratio is about 0.6 to 0.8 and it approaches unity for long photolysis.

Summarizing the material balance, reactions 6 and 7 account for about 70% of the decomposed CH_3I. Of the ethyl radical so produced, approximately 80% can be accounted for in the form of ethylene, formed via reactions 5 or 9 with secondary

photolysis. All of these reactions can occur within the matrix cage, confirming the usual observation that most of the chemistry brought on in condensed phase photolysis can be accounted for at the site of photolysis.

On the other hand, there is a discrepancy which suggests that reactions 6, 7, 5 and 9 do not account for all of the products. The remainders in the material balance indicate that some products probably remain undetected, possibly including free radical fragments from reactions 6 and/or 7.

These results may be compared with those obtained in the gas and liquid phases. Schultz and Taylor[9] concluded that the sole source of CH_4 in gas phase photolysis of CH_3I is reaction 8

$$CH_3{}^* + CH_3I = CH_4 + CH_2I \qquad (8)$$
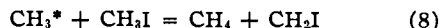
Accordingly, the gas phase ratio of $CH_4/\Delta(CH_3I)$ cannot exceed 0.5 (compared to the values near 0.9 in the solid matrices). This difference is consistent with the cage effect postulate.

Studying the pure liquid Hamil and Schuler[10] concluded that primary recombination is not important in fixing the low quantum yield for photolytic decomposition of CH_3I. Though this implies the cage effect is not operating to cause primary recombination, it does not contradict the present work since competing reactions such as (8) can occur *within* the cage in the pure liquid.

Hydrogen Abstraction from Partially Deuterated Hydrocarbons.—Quite apart from the relative yields of H and D abstraction, the data in Table III indicate the extent to which methane formation accounts for the decomposed methyl iodide. This is shown in the last column of Table III. The results for CH_3CD_3 are in reasonable agreement with those for C_2H_6: about 85% of the decomposed CH_3I appears as methane. The large contrast between the results with isobutane and isobutane-d is particularly interesting. For the isobutane-d, the low yield of total methane per mole of CH_3I decomposed might indicate exchange without reaction, forming CH_2DI.

Relative Rates: Hydrogen vs. Deuterium Abstraction from CH_3CD_3.—The experiment simplest to interpret is undoubtedly the abstraction from CH_3CD_3. The average mole ratio $(CH_4)/(CH_3D)$ is 1.16 ± 0.06 apparently higher than unity by an amount exceeding the experimental uncertainty. This difference gives a clue to the effective energy accessible to the methyl radical at the time of abstraction. The methyl radical cannot be "hot" with respect to the activation enthalpies for abstractions for then the ratio would be unity. Also the methyl radical cannot be "thermalized" to the ambient temperature, 20°K., or no abstraction would occur at all. We shall investigate the possibility of assigning an "effective temperature" to the methyl radical—one which accounts for the experimental $(CH_4)/(CH_3D)$ ratio.

The Energy of the CH_3 Fragment.—The ultraviolet spectrum of CH_3I was investigated by Goodeve and Porrett.[11] For absorption of a 2537 Å.

(9) R. Schultz and A. Taylor. *J. Chem. Phys.*, **18**, 194 (1950).

(10) R. Hamil and C. Schuler. *J. Am. Chem. Soc.*, **73**, 3466 (1951).

(11) D. Goodeve and C. Porret. *Proc. Roy. Soc. (London)*, **A165**, 31 (1938).

photon, the most probable event is transition to a repulsive state yielding $CH_3^* + I(^2P_{1/2})$ (* indicates a fragment possessing excess energy of translational and/or of other forms, a "hot" fragment.) After rupture of the C–I bond (54 kcal.), and excitation of the I atom (22 kcal.), conservation of energy and of momentum require that the methyl receives at most 32 kcal. translational energy, in which case the I atom receives 4 kcal. (2537 Å. = 112 kcal.).

This calculation is based on the neglect of possible excitation of vibrational degrees of freedom of CH_3. The evidence concerning the structure of the CH_3 radical indicates that methyl is planar, or very nearly so.[12,13] Considering the electronic excitation of CH_3I, the Franck–Condon principle dictates that the resulting CH_3 fragment be formed in a highly excited state of the out-of-plane bending mode of a planar structure. A rough estimate of the energy in this mode can be made. Excitation will tend to produce the planar CH_3 radical in vibrational states which have significant probability of reaching the tetrahedral angles. From the mean square displacement, we estimate that about 10 kcal./mole of vibrational excitation will be placed initially in this out-of-plane vibrational mode (an estimate chiefly limited in reliability by our guess of the out-of-plane force constant which was taken to be $0.25 \cdot 10^5$ dyne/cm., near that of BBr_3). Thus a significant fraction of the available energy (36 kcal.) is probably in vibrational degrees of freedom. It should be added that this energy could be quite accessible to abstraction processes since the CH_3 must assume a tetrahedral structure in the product.

The CH_3 radical is born, then, with 23–32 kcal./mole of translational energy and possibly 10 kcal./mole of vibrational energy. This defines a "hot" radical with reference to abstraction, as shown by the activation enthalpies shown in Table IV. Yet the results indicate a hydrogen/deuterium abstraction ratio appropriate to a lower temperature. In fact, the experimental ratio can be used

TABLE IV

ACTIVATION ENTHALPY FOR ABSTRACTION

Hydrocarbon	ΔH_H^*	ΔH_D^*
CD_4[14]	..	12.9
C_2H_6[16]	10.0	..
CH_3CD_3[16]	10.0	10.6
$(CH_3)_3CH$[16]	7.1 (tert.)	..
	10.0 (prim.)	..
$(CH_3)_4CD$[16]	10.0	7.7

(12) G. Herzberg and J. Shoosmith. Can. J. Phys., 34. 523 (1956).
(13) T. Cole. H. Pritchard. N. Davidson and H. McConnell. J. Molec. Phys.. 1. 406 (1958).

to define an "effective temperature" if we make the assumption that ΔS^* for hydrogen abstraction is the same as for deuterium abstraction. For the

$$\frac{k_H}{k_D} = \frac{(CH_4)}{(CH_3D)} = e^{-(\Delta H_H^* - \Delta H_D^*)/RT} \qquad (10)$$

experiments involving CH_3CD_3, we can insert $\Delta H_H^* - \Delta H_D^* = -0.6$ kcal. and $(CH_4)/(CH_3D) = 1.16 \pm 0.06$ into equation 10. We calculate, T_{eff} in the range 1500 to 3000°K.

The CH_4/CH_3D ratio found in the isobutane-d experiment provides a separate basis for calculating an effective temperature. Unfortunately a number of uncertainties becloud this estimate. Since the isobutane-d contains 30% isobutane, CH_4 can be formed either by the abstraction of the tertiary hydrogen of isobutane or a primary hydrogen from a methyl group from either $(CH_3)_3CH$ or $(CH_3)_3CD$. It is necessary to assume that ΔS^* is the same for all abstraction reactions, an assumption supported by arguments presented by Szwarc and Binks.[15] Finally, there is evidence that exchange may play a role in the isobutane-d experiments. With these reservations, then, we have calculated[17] from these data $T_{eff} \cong 1000°K$.

The absence of detectable CH_3D in experiment 2 (C_2H_6 and CD_4) provides one more datum, an upper limit on T_{eff}. Again appeal is made to the work of Szwarc and Binks[15] to justify assuming ΔS^* cancels. The temperature estimate so derived[17] is $T_{eff} < 700°K$.

Thus we have three values of CH_4/CH_3D which can be interpreted in terms of an effective temperature. Though the estimates are only in loose agreement, they permit an interesting conclusion. The methyl radical produced in reaction 6 reacts as a hot radical but after considerable moderation of its energy.

(14) F. Dainton and G. McElcheran. Trans. Faraday Soc.. 51. 657 (1955).
(15) M. Szwarc and J. Binks. Internat'l Union of Pure and Applied Chemistry. Paper presented at the Kekule Symposium. 262 (1958).
(16) F. Rice and T. Vanderslice. J. Am. Chem. Soc.. 80. 291 (1958).
(17) The rate of abstraction is assumed to be increased by a factor equal to the number of identical hydrogens. Thus a molecule of $(CH_3)_3CD$ provides nine sites for abstraction of H with $\Delta H^* = 10.0$ kcal./mole and one site for abstraction of D with $\Delta H^* = 7.7$ kcal./mole. The 30% of $(CH_3)_3CH$ also provides nine sites for abstraction of H with $\Delta H^* = 10.0$ kcal./mole and one site for abstraction of H with $\Delta H^* = 7.1$ kcal./mole. In experiment 2. the limit on the ratio CH_4/CH_3D was adjusted by a factor $(45/35) \cdot (4/6)$. compensating for the different values of M/C_2H_6 and M/CD_4 as well as for the number of atoms of each type.