

the hydrogen in the products involves one hydrogen atom of each of the two  $\text{CH}_2$  groups. From the structure proposed for 2,5-dihydrofuran, the distance between the position of the carbon atoms of the two  $\text{CH}_2$  groups (approx. 2.34–2.36 Å.) might seem large for the elimination of  $\text{H}_2$  from these groups. It is possible to envisage, as a conceivable mechanism, an initial migration of hydrogen in the ring to produce two adjacent  $\text{CH}_2$  groups (2,3-dihydrofuran). However, this mechanism seems to be ruled out because the thermal decomposition of 2,3-dihydrofuran<sup>14,2</sup> results mainly in the disappearance of the five-membered ring rather than a dehydrogenation to form furan (and hydrogen).

In the case of the dehydrogenation of 2,5-dihydrofuran, the route to the transition state may be a ring deformation in which the oxygen atom and the  $\text{CH}_2$  groups move out of a planar arrangement and the H atoms of the non-adjacent  $\text{CH}_2$  groups move closer together. Such a vibration may bring the hydrogen atoms into sufficiently close proximity to make the formation of molecular hydrogen possible. Formation of a transition state of this sort implies the loss of some vibrational freedom and results in a more rigid structure. This is con-

(14) C. L. Wilson, *J. Am. Chem. Soc.*, **69**, 3002 (1947).

sistent with the negative entropy of activation for the reaction. The somewhat analogous unimolecular decomposition of cyclopentene<sup>15</sup> also has a negative entropy of activation, ( $-2.7$  cal./deg. mole at  $500^\circ$ ) and the transition state may be formed by an analogous mechanism. In the decomposition of cyclopentene it is possible that the hydrogen molecule is produced from hydrogen atoms of adjacent methylene groups, but the possibility of formation of hydrogen from non-adjacent methylene groups has not been ruled out on the basis of the existing experimental results. Compared with the observed activation energy (58.8 kcal./mole) for the dehydrogenation of cyclopentene to cyclopentadiene, the activation energy for the dehydrogenation of 2,5-dihydrofuran is 10.3 kcal./mole lower. This may be the result of the greater resonance energy of furan (about 17.2 kcal./mole)<sup>16</sup> compared with that of 1,3-cyclopentadiene (2.9 kcal./mole).<sup>16</sup>

**Acknowledgment.**—The authors wish to thank Mr. Carl Whiteman, Jr., for making the infrared measurements and least squares calculations.

(15) D. W. Vanas and W. D. Walters, *ibid.*, **70**, 4035 (1948).

(16) G. W. Wheland, "Resonance in Organic Chemistry," John Wiley and Sons, Inc., New York, N. Y., 1955, p. 80 and p. 85.

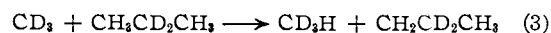
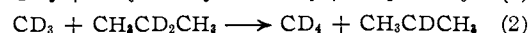
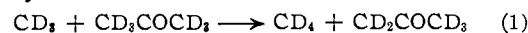
[CONTRIBUTION FROM THE NATIONAL BUREAU OF STANDARDS, WASHINGTON, D. C.]

## Photolysis of Acetone- $d_6$ in the Presence of Propane-2,2- $d_2$ . Decomposition of the $n$ -Propyl Radical

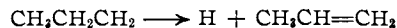
BY WILLIAM M. JACKSON AND J. R. MCNESBY

RECEIVED JUNE 3, 1961

Methyl- $d_3$  radicals generated by photolysis of acetone- $d_6$  react with acetone- $d_6$  and propane-2,2- $d_2$  to produce methane by the reactions



Ratios of rate constants obtained are approximately temperature independent and  $k_1/k_3 = 1.10$ ;  $k_2/k_3 = 0.58$ . Analogous ratios for  $\text{CH}_3$  radicals are indistinguishable from those for the  $\text{CD}_3$  species. Decomposition of  $n$ -propyl to H and propylene is found to proceed at a much lower rate than suggested by Kerr and Trotman-Dickenson. Consideration of kinetic and thermochemical evidence suggests the best values for the rate constants  $k_{3a}$  and  $k_{4a}$  are



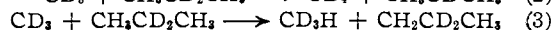
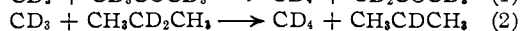
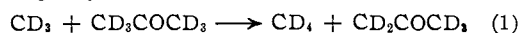
$$k_{3a} = 10^{14.1} \exp(-37,000/RT) \text{ sec.}^{-1} \quad (5a)$$



$$k_{4a} = 10^{13.9} \exp(-31,000/RT) \text{ sec.}^{-1} \quad (4a)$$

### Introduction

The present work was undertaken for the purpose of measuring the kinetics of abstraction reactions and to investigate reactions of propyl and isopropyl radicals. The methane producing reactions when acetone- $d_6$  is photolyzed in the presence of  $\text{CH}_3\text{CD}_2\text{CH}_3$  are



The  $n$ -propyl radical produced in (3) decomposes to  $\text{CH}_3$  radicals and ethylene, but the former do not affect the  $\text{CD}_4$  and  $\text{CD}_3\text{H}$ . In the early stages of reaction

$$[\text{CD}_4]/[\text{CD}_3\text{H}] = k_1[\text{Ad}_6]/k_3[\text{Pd}_2] + k_2/k_3 \quad 1$$

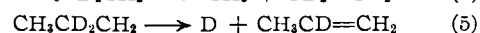
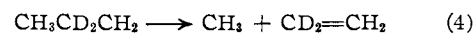
where  $[\text{Ad}_6]$  and  $[\text{Pd}_2]$  refer to the concentrations of acetone- $d_6$  and propane-2,2- $d_2$ , respectively.

The measurement of  $[\text{CD}_4]/[\text{CD}_3\text{H}]$  provides a means of evaluating  $k_1/k_3$  and  $k_2/k_3$ . These ratios may be reduced further by carrying out the measurements at different temperatures.

$$k_1/k_3 = (A_1/A_3) \exp[(E_3 - E_1)/(RT)] \quad 2$$

$$k_2/k_3 = (A_2/A_3) \exp[(E_3 - E_2)/(RT)] \quad 3$$

The problem of the kinetics of the decomposition of  $n$ -propyl to form propylene has been studied by examination of the relative rates of the two decomposition reactions.



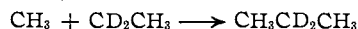
### Experimental

**I. Apparatus.**—The light source was the full arc of a medium pressure mercury lamp. A filter was used to remove radiation below 2200 Å. The apparatus consisted of a cylindrical quartz reaction vessel, of 40 cc. capacity,

centrally located in an aluminum block furnace. All valves were of the brass or monel bellows type, no stopcocks being used.

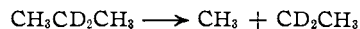
**II. Chemicals.**—A. Acetone- $d_6$  was obtained from Merck & Co. Ltd., Montreal, and its photolysis gave  $\text{CD}_3\text{H}/\text{CD}_4 = 0.04$  at  $250^\circ$  and  $400^\circ$ .

B. Propane-2,2- $d_2$ : Commercial supplies of  $\text{CH}_3\text{CD}_2\text{CH}_3$  proved to be unsatisfactory and we employed a photochemical synthetic method for its preparation. Diethyl ketone was deuteriated in the four alpha positions.<sup>1</sup> Finally it was vacuum distilled and a middle cut was retained. Mass spectrometer analysis of the resulting diethyl ketone indicated 97%  $\text{CH}_3\text{CD}_2\text{COCD}_2\text{CH}_3$  and 3%  $\text{CH}_3\text{CDHCOCD}_2\text{CH}_3$ . The ethyl radicals produced in the photolysis of this material consisted, therefore, of 1.5%  $\text{CH}_3\text{CDH}$  and 98.5%  $\text{CH}_3\text{CD}_2$ . The photolysis of a mixture of 30 mm. of diethyl ketone- $d_4$  and 70 mm. of acetone at room temperature produced propane-2,2- $d_2$  by the reaction

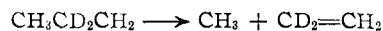


Twenty such photolyses were made for 2 hr. each in an air cooled one liter quartz flask using a medium pressure mercury arc as the light source. The propane fraction of the reaction products was separated and trapped by gas chromatography using a two meter silica gel column at  $90^\circ$ . The propane-2,2- $d_2$  then was distilled through a  $\text{P}_2\text{O}_5$  trap, frozen and pumped. From the purity of the diethyl ketone- $d_4$ , it is estimated that the propane composition was 98.5%  $\text{CH}_3\text{CD}_2\text{CH}_3$  and 1.5%  $\text{CH}_3\text{CDHCH}_3$ .

Location of D atoms in Propane: When propane is pyrolyzed, methyl radicals are formed in the primary act

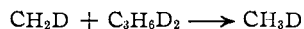
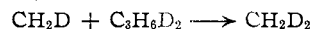


Propyl radicals produced subsequent to the primary process decompose further to produce additional methyl radicals.

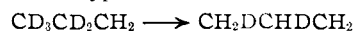


If any of the D atoms are located in primary positions,  $\text{CH}_2\text{D}$  radicals will be formed.

These  $\text{CH}_2\text{D}$  radicals are detected easily since they abstract D from propane- $d_2$  about half as fast as they do H.



While  $\text{CH}_3\text{D}$  can be formed from  $\text{CH}_3$  radicals,  $\text{CH}_2\text{D}_2$  can only come from  $\text{CH}_2\text{D}$ . Several commercial samples of material asserted to be  $\text{CH}_3\text{CD}_2\text{CH}_3$  gave rather large amounts of  $\text{CH}_2\text{D}_2$  upon pyrolysis. If the propane were in fact pure  $\text{CH}_3\text{CD}_2\text{CH}_3$ , this observation would have important implications regarding the possibility of homogeneous reactions of the type



Such scrambling reactions would, of course, render an analysis of the isotopic methanes meaningless in a study of methyl radical abstraction reactions.

Pyrolysis of the photochemically prepared  $\text{CH}_3\text{CD}_2\text{CH}_3$  produced no detectable  $\text{CH}_2\text{D}_2$  and the inference drawn was that no primary D atoms existed in the material. Further, on the basis that the mass spectral sensitivity at parent mass 46 was indistinguishable from that of propane at mass 44, it was concluded that propane and propane-1- $d$  were absent and the material was about 99%  $\text{CH}_3\text{CD}_2\text{CH}_3$ . Subsequently, an experimental sample of propane-2,2- $d_2$  was obtained from Merck and Co. Ltd., Montreal, whose mass spectrum was indistinguishable from that of our standard synthetic material and whose pyrolysis produced no  $\text{CH}_2\text{D}_2$ . It was upon this material that the photochemical reactions were carried out. Gas chromatographic analysis revealed no impurities higher than 0.1%.

**III. Procedure.**—Mixtures of acetone- $d_6$  and propane-2,2- $d_2$  were prepared and allowed to mix for at least 24 hr. Photolyses were carried out at total pressures of about 50 mm. so that less than 0.5% of either component was consumed. Reaction times were from 3-15 minutes. The resulting reaction mixture was transferred, by means of a Toepler pump, through a liquid nitrogen trap into a sample flask. The contents of the latter were analyzed on a Consolidated Electro-dynamics 21-620 mass spectrometer

for methane and hydrogen. The mass spectra of  $\text{CH}_4$  and  $\text{CD}_4$  were measured and they compared very well with the published values in the mass range 12-20.<sup>2</sup>

The published cracking patterns of  $\text{CD}_3\text{H}$  and  $\text{CH}_3\text{D}$  were, therefore, considered to be accurate for our mass spectrometer and they were used in the analysis of the isotopic methanes. The ion abundances of the methanes at masses 2, 3 and 4 were quite different from the published values and measured cracking patterns of somewhat impure isotopic methanes were used in assessing the contribution of the methanes to masses 2, 3 and 4.

The mass spectrum of the photochemically prepared propane-2,2- $d_2$  is compared with that of propane in Table I.

TABLE I  
MASS SPECTRA<sup>a</sup> OF PHOTOCHEMICALLY PREPARED PROPANE-2,2- $d_2$  AND OF PROPANE

$m/e$	Relative abundance of $\text{CH}_3\text{CD}_2\text{CH}_3$	$\text{CH}_3\text{CH}_2\text{CH}_3$
2	1.26	0.34
3	0.10	..
4	..	..
12	0.48	.47
13	0.68	.73
14	1.64	1.75
15	3.54	4.96
16	1.59	0.13
17	0.44	..
18	.03	..
19	.55	1.45
19.5	.72	0.76
20	.66	1.33
20.5	.64	0.28
21	.40	.0
21.5	.10	.0
22	.01	.0
23	..	..
24	.14	.15
25	.32	.73
26	2.13	7.14
27	10.58	36.35
28	27.70	58.08
29	26.88	100.00
30	56.19	2.06
31	100.00	..
32	2.36	..
33	0.04	..
34	..	..
35	..	..
36	0.44	0.56
37	1.48	2.94
38	2.27	4.23
39	5.39	13.13
40	6.74	1.85
41	3.49	11.33
42	5.14	3.86
43	4.95	20.77
44	6.83	22.10
45	3.70	0.75
46	22.32	..
47	0.82	..

<sup>a</sup> Consolidated Electro-dynamics Mass Spectrometer 21-620, ion current 20  $\mu\text{amp}$ . Sensitivity at mass 31 for propane-2,2- $d_2$ /Sensitivity at mass 29 for propane = 1.015.

## Results

### I. Methane Analysis in Photolysis of Acetone- $d_6$ in the Presence of Propane-2,2- $d_2$ .—The results

(1) J. R. McNesby and A. S. Gordon, *J. Phys. Chem.*, **59**, 988 (1955).

(2) R. L. Mohler, V. H. Dibeler and E. Quinn, *J. Research Natl. Bur. Standards*, **61**, 171 (1958).

TABLE II

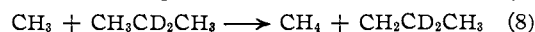
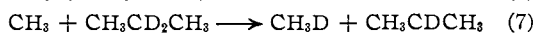
METHANE-HYDROGEN ANALYSIS IN THE PHOTOLYSIS OF ACETONE- $d_6$  IN THE PRESENCE OF PROPANE-2,2- $d_2$ 

$\frac{Ad_6}{Pd_2}$	Temp., °C.	$(CD_4/CD_3H)$ corr.	$\frac{CH_4 + CH_3D}{CD_3H}$	$CH_3D/CH_4$	HD/ $H_2$	$H_2/CH_4$	$\frac{CH_2D_2}{CH_4}$	$\frac{D_2}{CH_3D}$
0.25	295.9	0.82	0.74	0.84	..	0.040	0.084	0.00
.25	305.7	.81	1.02	.80	..	.046	.037	.00
.25	344.4	.84	2.37	.79	..	.18	.015	.00
.25	437.9	.87	9.10	.81	1.0	.50	.0	.015
.25	446.0	.89	10.07	.83	1.0	.70	.014	.022
.36	282.2	.98	0.45	1.03	..	...	....	.00
.36	322.5	.96	1.38	0.96	..	.16	.036	.00
.36	336.7	1.01	1.55	.97	..	.13	.052	.00
.36	393.9	1.05	3.45	.98	1.02	.27	-.014	.007
.36	441.0	1.04	7.77	.99	1.10	.51	.007	.017
.77 <sup>a</sup>	303.6	1.37	1.42	1.24	..	...	...	...
.77	305.5	1.40	0.75	1.43	..	.11	-.057	.00
.77	354.3	1.41	2.02	1.38	1.35	.17	.033	.014
.77	416.2	1.42	4.33	1.29	0.94	.74	-.013	.00
.77	451.7	1.40	5.40	1.34	1.07	.98	.021	.036
1.15	301.6	1.845	0.56	1.83	..	...	-.10	.00
1.15	337.7	1.875	1.18	1.80	..	.14	-.046	.00
1.15	382.9	1.835	2.34	1.79	0.93	.45	.038	.006
1.15	420.3	1.875	3.56	1.71	1.40	.49	-.042	.009

<sup>a</sup> Intensity reduced to  $1/200$  of other experiments. Absence of a number means the amount of HD or  $D_2$  was too small for meaningful measurements.

are shown in Table II. Since the admission of small amounts of water vapor was inevitable in the mass spectral analyses, a somewhat uncertain water background had to be subtracted. This was done after analysis by stopping the sweep on top of mass 18 and then rapidly pumping the sample from the mass spectrometer. The  $CH_2D_2$  is pumped away very rapidly while water is pumped much more slowly. A discontinuity in the signal results and from it is obtained the contribution of  $H_2O$  to mass 18. This background was always small, the random positive and negative residuals at mass 18 reflecting the uncertainty in the water correction. This is included in Table II as  $CH_2D_2/CH_4$ . Thus the evidence for the production of  $CH_2D_2$  is negative.

The methanes,  $CD_4$  and  $CD_3H$ , are formed by reactions 1, 2 and 3. Methyl radicals are formed by (4). The other methanes,  $CH_3D$  and  $CH_4$ , are formed by the reactions



Measurement of the product ratios  $[CD_4]/[CD_3H]$  and  $[CH_3D]/[CH_4]$  gives rate constants according to equations 1 and 4.

$$[CH_3D]/[CH_4] = \frac{k_6[Ad_7]}{k_8[Pd_2]} + k_7/k_8 \quad 4$$

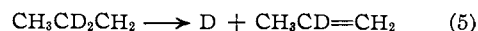
It was necessary to correct the  $CD_3H$  for the small amount of  $CD_3H$  formed because of the acetone- $d_6$  impurity in the acetone- $d_6$ . The relative rate of abstraction of D and H from propane-2,2- $d_2$  is about 0.5:1 and photolysis of acetone- $d_6$  gives  $[CD_3H]/[CD_4] = 0.04$ . The correction was made by using the equation

$$[CD_4]/[CD_3H]_{\text{corr.}} = \frac{1}{\left(\frac{[CD_3H]}{[CD_4]}\right)_{\text{obsd.}} - \frac{0.04}{1 + 0.50 [Pd_2]/[Ad_6]}}$$

Under the conditions of these experiments it did

not seem likely that disproportionation reactions could contribute to the formation of  $CD_3H$  or  $CD_4$ . This expectation was confirmed by reducing the light intensity by means of wire mesh screens to  $1/200$  of the usual intensity. Under these conditions, disproportionations would be greatly reduced if they had been occurring at the higher intensities. The result in Table II shows that  $[CD_4]/[CD_3H]$  is independent of intensity and that disproportionation as a source of  $CD_3H$  or  $CD_4$  is not important. Since the error in measurement of  $[CD_4]/[CD_3H]$  appears to be about  $\pm 3\%$ , it is difficult to state with conviction that the data show any trend with temperature. For this reason, it has been concluded that the ratio is independent of temperature from 300 to 450°. It is evident that no trend of  $[CH_3D]/[CH_4]$  with temperature is observed.

II. Elimination of the D Atom from *n*-Propyl-2,2- $d_2$ .—It is of interest to evaluate the importance of the reaction



As shown, the methyl radical abstracts H about 1.5 times as rapidly as D, and it is reasonable to expect that D atoms will not show greater discrimination. They should abstract H and D in the ratio 3:2. It becomes possible to compare the rate constant,  $k_5$ , with  $k_4$  (decomposition of *n*-propyl to methyl and ethylene) by measuring the relative number of  $CH_3$  radicals and D atoms produced. Now, at high temperatures nearly all  $CH_3$  radicals appear as  $CH_3D$  and  $CH_4$ , while D appears as  $D_2$  and HD. To measure the relative rates of production of  $CH_3$  and D it is only necessary to use the relation

$$\frac{R_D}{R_{CH_3}} = \frac{2.5[D_2]}{([CH_3D] + [CH_4])} = k_5/k_4 \quad 5$$

The results for the thermal decomposition of the photochemically prepared propane-2,2- $d_2$  are presented in Table IV. Along with these results a few additional experiments are reported in Table V in

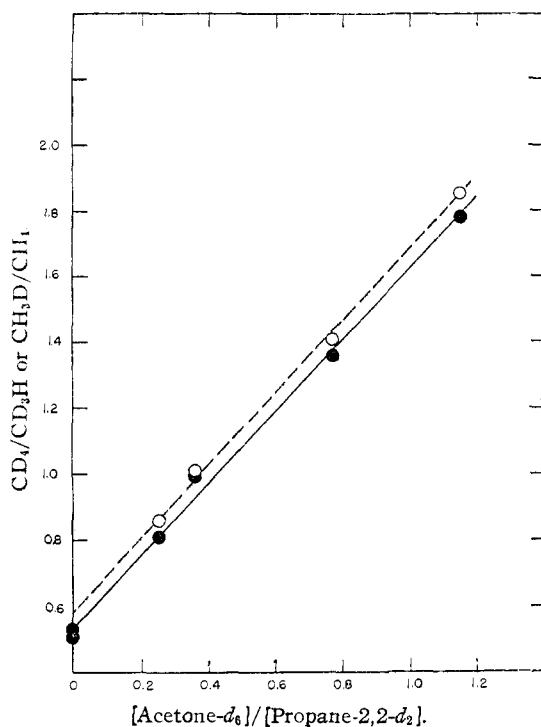


Fig. 1.—Abstraction of H and D by methyl radicals from a mixture of acetone- $d_6$  and propane-2,2- $d_2$ : ○,  $[CD_4]/[CD_3H]$ ; ●,  $(CH_3D)/[CH_4]$ .

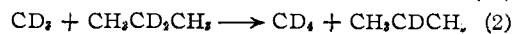
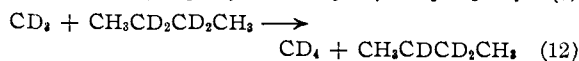
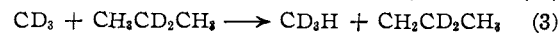
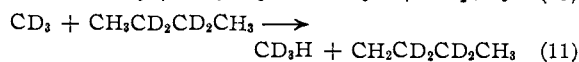
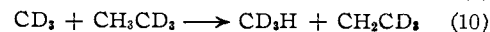
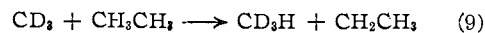
which we used incompletely deuteriated acetone and the photochemically prepared propane-2,2- $d_2$ . These experiments were not useful in determining rate constants for methyl abstracting H and D from propane but are quite valid for measurement of  $k_6/k_4$ .

### Discussion

**I. Reaction of Methyl Radicals with Propane-2,2- $d_2$ .**—The intercept of the plot of  $[CH_3D]/[CH_4]$  vs.  $[Ad_6]/[Pd_2]$  according to equation 4 should be equal to  $k_7/k_8$ . Now, if propane-2,2- $d_2$  is pyrolyzed and the mechanism of methane formation is the same as before,  $[CH_3D]/[CH_4]$  should give, directly, the intercept  $k_7/k_8$  observed in the photochemical experiments. That this is so is shown in Fig. 1 where the filled circles represent average values of  $[CH_3D]/[CH_4]$  at various compositions,  $[Ad_6]/[Pd_2]$  and the open circles are  $[CD_4]/[CD_3H]$ .

In order to have some idea of chain lengths in propane decomposition, we may define chain length as the number of  $CH_3$  radicals released per  $n$ -propyl radical formed, *i.e.*, approximately  $([CH_4] + [CH_3D])/[CD_3H]$ . The actual situation is far more complicated than this for isopropyl radicals may also participate and hydrogen may be formed in chain propagating steps. Nevertheless, it is evident from the data in Table II that the crude approximation,  $([CH_4] + [CH_3D])/[CD_3H]$ , increases very rapidly as  $[Ad_6]/[Pd_2]$  decreases. Also the ratio increases rapidly with increasing temperature. The chain lengths in the absence of acetone- $d_6$  are difficult to obtain by extrapolation, but it is apparent that they must be very long, probably of the order of hundreds at pyrolysis temperatures.

**II. General Considerations in Methyl Radical Metathesis.**—It is suggested that primary H is abstracted from  $n$ -alkanes at a rate which is independent of the nature of the alkane and depends only upon the density of abstractable H atoms. A similar hypothesis may be put forth for secondary and tertiary abstractions. There is now enough information to test this idea for the cases of primary and secondary H abstractions. Consider the series of reactions



The approximate relationships which should exist are

$$\frac{k_9}{k_1} = \frac{k_{11}}{k_1} = \frac{k_2}{k_1} = \frac{2k_{10}}{k_1} \quad \frac{6}{7}$$

$$\frac{k_{12}}{k_1} = \frac{2k_2}{k_1} \quad \frac{7}{9}$$

Division of 6 and 7 by  $k_1$  results in 8 and 9.

$$\frac{k_9/k_1}{k_{12}/k_1} = \frac{k_{11}/k_1}{2k_2/k_1} = \frac{k_2/k_1}{2k_{10}/k_1} \quad \frac{8}{9}$$

If this hypothesis is correct, these relationships should be obeyed independent of temperature. The results of these studies are collected in Table III.

TABLE III

RELATIVE RATE CONSTANTS FOR H AND D ABSTRACTION FOR ALKANES<sup>a</sup>

	Ratio/ Temp., °C.	300	350	400	450	$E_a$ , kcal.	Ref.
$CH_3CH_3$	$k_9/k_1$	1.00	0.99	0.96	0.95	11.5	3-5
$CH_3^*CD_2CD_2^*CH_3$	$k_{11}/k_1$	..	.93	.91	.93	11.4	6
$CH_3CD_2^*CH_3$	$k_2/k_1$	0.91	.91	.91	.91	11.3	..
$CH_3^*CD_2$	$2k_{10}/k_1$	0.94	.98	1.00	1.02	11.6	5
$CH_3^*CD_2^*CD_2^*CH_3$	$k_{12}/k_1$	..	1.00	0.96	1.03	11.4	6
$CH_3CD_2^*CH_3$	$2k_2/k_1$	1.05	1.05	1.05	1.05	11.3	..

<sup>a</sup> Values for propane-2,2- $d_2$  are based on the conclusion in this paper that no temperature coefficient exists for  $k_2/k_1$  or  $k_8/k_1$ . The starred positions are those at which abstraction occurs.  $E_a$  is the activation energy for abstraction of H or D from the alkane.

Because of the differences in collision diameter between ethane, propane and  $n$ -butane, exact agreement with the hypothesis is not expected, but in view of these uncertainties, the agreement is excellent. Thus, for the abstraction of primary H,  $k_p/k_1 = 0.98 \pm 0.07$  from 300 to 450°. Abstraction of secondary D is also seen to depend only upon the population of D atoms in the molecule.

It is of interest that  $A_2/A_3 = 0.58$ , the  $A$ 's being the Arrhenius pre-exponential factors, while

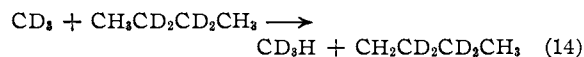
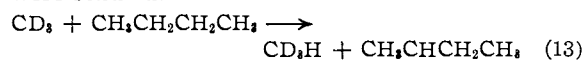
(3) J. R. McNesby and A. S. Gordon, *J. Am. Chem. Soc.*, **77**, 4719 (1955).

(4) M. H. J. Wijnen, *J. Chem. Phys.*, **23**, 1357 (1955).

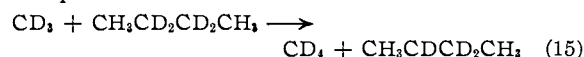
(5) J. R. McNesby, *J. Phys. Chem.*, **64**, 1671 (1960).

(6) J. R. McNesby and A. S. Gordon, *J. Am. Chem. Soc.*, **78**, 3570 (1956).

the expected value is 0.33. In the reaction of  $CD_3$  radicals with  $n$ -butane reactions (13) and (14) were studied.<sup>5</sup>



In this case  $A_{13}/A_{14} = 0.67$  as expected on purely statistical grounds. However, when (14) was compared with



it was found that  $A_{15}/A_{14} = 1.06$ . The fact that  $A_2/A_3$  and  $A_{15}/A_{14}$  substantially exceed the statistical expectation can be explained by invoking quantum mechanical tunnelling. The magnitude of the tunnelling effect is very close to that predicted by the theoretical treatment of Johnston and Rapp.<sup>7</sup>

**III. Bond Strength Implications.**—The problem of measuring differences in bond strengths between various C–H bonds in hydrocarbons has not been solved with any success. The precision of the various methods rarely exceeds  $\pm 2$  kcal., and for this reason it is extremely difficult to know whether the C–H bond strength in ethane is higher or lower than that in other molecules. The application of the Evans–Polanyi rule<sup>8</sup> is perhaps the best indication of bond strength differences. In its simplest form the rule may be written

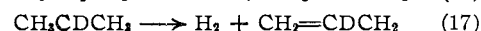
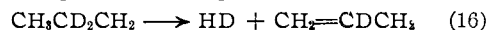
$$\Delta E_a = \alpha \Delta D$$

That is, the difference in activation energies for two analogous reactions is proportional to the difference in the dissociation energies of the broken bonds. The value of  $\alpha$  is not known because of our ignorance of  $\Delta D$  but is probably  $0.5 \pm 0.2$ . In any case, if  $\Delta E_a = 0$ ,  $\Delta D = 0$ . Since  $\Delta E_a$  in the cases of ethane +  $p$ -propane and ethane +  $p$ -butane is zero (the prefix  $p$ - signifies abstraction of primary H), the conclusion is that the bond strengths  $D(C_2H_5-H)$ ,  $D(n-C_3H_7-H)$  and  $D(n-C_4H_9-H)$  are all equal, *i.e.*, 97 kcal.<sup>9,10</sup> Further, since the energy of activation for abstraction of secondary D in  $CH_3CD_2CD_2CH_3$  is the same as in  $CH_3CD_2CH_3$ , it may be concluded that  $D(i-C_3H_7-H) = D(s-C_4H_9-H)$ .

The Evans–Polanyi rule gives<sup>8</sup>  $D(s-C_4H_9-H) = D(i-C_3H_7-H) = 93$  kcal. It has been suggested<sup>11</sup> that  $D(n-C_3H_7-H) = 102.7$  kcal. from thermochemical arguments. Our work does not support this nor does it support a value of 104.1 kcal. deduced for  $D(i-C_3H_7-H)$ .<sup>11</sup>

**IV. Decomposition of  $n$ -Propyl. A. Molecular Hydrogen Elimination.**—Until recently it had been assumed that in a system containing  $n$ -propyl and  $i$ -propyl radicals, hydrogen was produced by the radicals expelling atomic hydrogen which subsequently abstracted H from the parent hydro-

carbon. Gordon and Smith<sup>12</sup> have presented evidence for an alternative mechanism not involving hydrogen atoms. Their suggested mechanism corresponds, in the present case, to



While our HD/ $H_2$  ratios show considerable scatter, they seem to vary little with the composition,  $[Ad_6]/[Pd_2]$ . Because the HD/ $H_2$  ratios in the pyrolysis of pure propane-2,2- $d_2$  (Table IV) are smaller than when mixtures of acetone- $d_6$  and propane-2,2- $d_2$  are the reactants, we conclude that some H atoms are formed from  $i$ -propyl radicals. The relative importance of the atomic and molecular mechanisms is difficult to assess, but it must be concluded that our results are not inconsistent with the molecular mechanism.

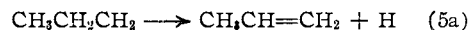
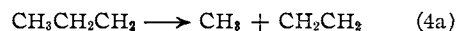
TABLE IV

PYROLYSIS OF PROPANE-2,2- $d_2$ -NBS SYNTHETIC COMPOUND

Temp., °C. <sup>a</sup>	HD/ H <sub>2</sub>	$k_5/k_4 =$ $2.5[D_2]/([CH_3D] +$ $[CH_4])$	$k_{5a}/k_{4a}$	$(k_{5a}/k_{4a})_{TD}$
508 P	0.76	0.017	0.04	0.15
505 Q	.74	.009	.02	.15
542 P	.67	.024	.06	.19

<sup>a</sup> P Pyrex reaction vessel; Q quartz reaction vessel;  $(k_{5a}/k_{4a})_{TD}$  from ref. 10.

**B. Atomic Hydrogen Elimination.**—It is likely that an isotope effect exists for reaction 5 while nearly none is expected for reaction 4. If we wish to compare the reactions



it is necessary to correct (5a) for the deuterium isotope effect. While no direct measurements have been made, it seems likely that the relation  $k_{5a}/k_5 = \exp(1500/RT)$  is a generous estimate. Values of  $k_{5a}/k_{4a}$  calculated from the data of Kerr and Trotman-Dickenson<sup>11</sup> are included in Table IV for comparison with our results. Estimates have been made of  $k_{5a}/k_5$  on a similar basis in the experiments on the photolysis of acetone- $d_6$  in the presence of propane-2,2- $d_2$ .

The data in Table V show that  $k_{5a}/k_{4a}$  is always small but that considerable scatter exists due to such factors as the rather large subtractions to be made from mass 4 due to the contribution from  $CD_4$  and  $CD_3H$ . These subtractions do not complicate the picture in the pyrolysis results in Table IV, and it is the latter that are considered to be most reliable. At 500° a realistic estimate is  $k_{5a}/k_{4a} = 0.03$ . This is to be compared with the value calculated from the results of Kerr and Trotman-Dickenson,<sup>11</sup>  $k_{5a}/k_{4a} = 0.15$ . The conclusion is that decomposition by (5a) is much less important than Kerr and Trotman-Dickenson suggest. A rather serious objection can be raised to their interpretation of  $n$ -butyraldehyde photolysis, namely, that their estimate of  $k_{5a}/k_{4a}$  depends upon their assumption that the radical  $CH_3CHCH_2CHO$  has a very low activation energy for decomposition. If this assumption is false, the increasing amounts

(12) A. S. Gordon and S. R. Smith, *J. Chem. Phys.*, **34**, 331 (1961).

(7) H. S. Johnston and D. Rapp, *ibid.*, **33**, 1 (1961).

(8) M. G. Evans and M. Polanyi, *Trans. Faraday Soc.*, **34**, 11 (1938).

(9) T. L. Cottrell, "The Strength of Chemical Bonds," Butterworths, London, 1938.

(10) A. F. Trotman-Dickenson, "Gas Kinetics," Butterworths, London, 1955.

(11) J. A. Kerr and A. F. Trotman-Dickenson, *Trans. Faraday Soc.*, **55**, 575 (1959).

of propylene observed at higher temperatures can be attributed to the progressively faster decomposition of the  $\text{CH}_3\text{CHCH}_2\text{CHO}$  radical and not to the decomposition of the *n*-propyl radical *via* (5a).

TABLE V  
DECOMPOSITION OF  $\text{CH}_3\text{CD}_2\text{CH}_2$  RADICAL

Temp., °C.	[ <i>Ad</i> ]/[ <i>Pd</i> ] <sub>2</sub>	$k_3/k_4$	$k_{5a}/k_{4a}$	$(k_{5a}/k_{4a})_{TD}$
383 <sup>b</sup>	1.15	0.012	0.031	0.047
380	0.41	.00	.00	.044
394 <sup>b</sup>	.36	.007	.02	.051
400	.20	.00	.00	.055
420 <sup>b</sup>	1.15	.012	.031	.047
434	0.41	.016	.04	.079
438 <sup>b</sup>	.25	.012	.03	.083
441 <sup>b</sup>	.36	.017	.04	.085
446 <sup>b</sup>	.25	.018	.05	.087
452 <sup>b</sup>	.77	.036	.094	.090
466	.20	.024	.06	.10
480	.41	.024	.06	.12
480 <sup>a</sup>	.41	.024	.06	.12

<sup>a</sup> Thermal reaction. <sup>b</sup> Merck propane-2,2-*d*<sub>2</sub>.

**C. Appraisal of Kinetics of Thermal Decomposition of *n*-Propyl.**—We have concluded that  $D(i\text{-C}_3\text{H}_7\text{-H}) = 93$  kcal. It is generally agreed<sup>10</sup> that  $D(\text{CH}_3\text{-C}_2\text{H}_5) = 82$  kcal. Then, if it is recognized (as Semenov suggests) that the  $\pi$  bond strengths in ethylene and propylene are equal and that the thermochemistry of the addition of H to ethylene and propylene (to form isopropyl) are identical, it follows that

$$\Delta H_{5a}^0 - \Delta H_{4a}^0 = 11 \text{ kcal.}$$

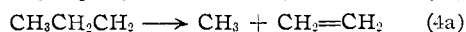
Since the activation energy of (– 5a) is 5 kcal. less than that<sup>9</sup> for (– 4a)

$$E_{5a} - E_{4a} = 6 \text{ kcal.}$$

Now if we adopt our value of  $k_{5a}/k_{4a} = 0.03$  at 500° and use  $E_{5a} - E_{4a} = 6$  kcal., it is possible to calculate  $A_{5a}/A_{4a}$ . The result is  $A_{5a}/A_{4a} = 1.5$ .

The conclusion of Kerr and Trotman-Dickenson<sup>11</sup> that  $A_{5a}/A_{4a} = 10^{1.9}$  is a necessary consequence of reaction 5a being so rapid and their assumption of a very high dissociation energy for secondary H in propane (104.1 kcal.).

Consider the two reactions in question



Of first importance is the difference in the standard enthalpy change in the two reactions. Following Semenov<sup>13</sup> these assumptions are made: (a) The

energy of the  $\pi$  bond is identical in ethylene and propylene. (b) The difference in standard enthalpies of (5a) and (4a) is equal to the difference in bond dissociation energies,  $D(i\text{-C}_3\text{H}_7\text{-H}) - D(\text{C}_2\text{H}_5\text{-CH}_3)$ . (c) The activation energy for addition of H to propylene to form *n*-propyl is 2 kcal. (d) The activation energy for addition of  $\text{CH}_3$  to ethylene is 7 kcal.<sup>10</sup> The major question is the secondary bond strength in propane. The suggestion of Kerr and Trotman-Dickenson that  $D(i\text{-C}_3\text{H}_7\text{-H}) = 104.1$  kcal. seems unreasonably high in view of our finding that secondary *D* is abstracted from propane-2,2-*d*<sub>2</sub> with about the same activation energy as primary H, since the bond strength of primary H is about 97 kcal. Kerr and Trotman-Dickenson have shown that

$$E_{4a} - E_{-4a} = \Delta H_f^0(\text{CH}_3) + \Delta H_f^0(\text{C}_2\text{H}_4) - \Delta H_f^0(\text{C}_3\text{H}_8) - D(n\text{-C}_3\text{H}_7\text{-H}) + \Delta H_f^0(\text{H}) \quad 11$$

$$D(n\text{-C}_3\text{H}_7\text{-H}) = E_{-4a} - E_{4a} + 32.5 + 12.5 + 24.8 + 52 = 121.8 + E_{-4a} - E_{4a} \quad 12$$

Now, Semenov has shown that  $\Delta H_{4a}^0$  may be calculated from the breaking of the C–C bond (82 kcal.) and the formation of a  $\pi$  bond (58 kcal.). Thus  $\Delta H_{4a}^0 = 24$  kcal. It follows that

$$E_{5a} - E_{-4a} = 24 \text{ kcal.}$$

Thus  $D(n\text{-C}_3\text{H}_7\text{-H}) = 98$  kcal., a value very close to that generally agreed upon for  $D(\text{C}_2\text{H}_5\text{-H})$ . If these calculations are valid, it is necessary that  $E_{4a} = 31$  kcal. Assuming that the mean absolute value of  $k_{4a}$  as measured by Kerr and Trotman-Dickenson is correct but that the temperature coefficient is in error and should correspond to 31 kcal., the rate constant becomes

$$k_{4a} = 10^{13.9} \exp(-31,000/RT) \text{ sec.}^{-1} \quad 13$$

From our results

$$K_{5a}/k_{4a} = 1.5 \exp(-6000/RT)$$

and

$$k_{5a} = 10^{14.1} \exp(-37,000/RT) \text{ sec.}^{-1} \quad 14$$

It is our position that these values of  $k_{4a}$  and  $k_{5a}$  are presently in best agreement with the total thermochemical and kinetic evidence. The value of  $k_{4a} = 2.85 \times 10^{13} \exp(-34,900/RT) \text{ sec.}^{-1}$  obtained by Calvert and Sleppy<sup>14</sup> is subject to some uncertainty because of the contribution of the  $\text{CH}_2\text{CH}_2\text{CH}_2\text{CHO}$  radical to the ethylene product and because of the experimental error which may place their value for  $k_{4a}$  close to ours. Certainly, as Calvert and Sleppy point out, the older values of 19–20 kcal. for  $E_{4a}$  are badly in error.

(13) N. N. Semenov, "Some Problems in Chemical Kinetics and Reactions," Vol. 1, Pergamon Press, New York, N. Y., 1958, p. 59.

(14) J. G. Calvert and W. C. Sleppy, *J. Am. Chem. Soc.*, **81**, 1541 (1959).