JOURNAL OF THE
AMERICAN CHEMICAL SOCIETY

VOLUME 84 SEPTEMBER 28, 1962 NUMBER 18

PHYSICAL AND INORGANIC CHEMISTRY

[CONTRIBUTION FROM THE GIBBS CHEMICAL LABORATORY, HARVARD UNIVERSITY, CAMBRIDGE, MASS.]

The Reactions of Methylene. VI. The Addition of Methylene to Hydrogen and Methane

BY JERRY A. BELL AND G. B. KISTIAKOWSKY

RECEIVED FEBRUARY 2, 1962

The initial step in the reaction of methylene with hydrogen and methane is primarily an addition to form, respectively, vibrationally excited methane and ethane. These activated molecules are either stabilized by collisions or dissociate to give free radical fragments. The activated methane dissociates to a methyl radical and a hydrogen atom and the ethane to two methyl radicals. The reaction with hydrogen is approximately one-sixth as rapid as reaction with carbon–carbon double bonds. Calculations based on the mode of decay of the excited methane molecule give $D(CH_2\text{–}H) \geq 104$ kcal./mole. Comparison of the lifetime of the ethane formed from methylene and methane with that produced by association of methyl radicals yields a second value, $D(CH_2\text{–}H) = 103 \pm 6$ kcal./mole. Combination of the present results with others recently obtained spectroscopically and thermochemically suggest $D(CH_2\text{–}H) = 105 \pm 3$ kcal./mole and, hence, $D(CH\text{–}H) = 108 \pm 3$ kcal./mole.

Introduction

The mechanism of the reaction of methylene with hydrogen is unsettled. Chanmugam and Burton[1] (C and B) photolyzed ketene and deuterium mixtures as well as ketene and hydrogen. On the basis of mass spectrometric analyses of the products they concluded that both the direct addition to give methane and the abstraction of a hydrogen atom to give a methyl radical occur. At room temperature the abstraction reaction is negligible compared to the addition reaction.

Gesser and Steacie[2] (G and S), however, observed no methane at room temperature in the photolysis of ketene and hydrogen mixtures. On the other hand, they observed the formation of methyl ethyl ketone at higher temperatures where methane was also observed. They proposed an abstraction mechanism involving methyl radicals

$$CH_2CO + h\nu \longrightarrow CH_2 + CO \qquad (1a)$$

$$CH_2 + CH_2CO \longrightarrow C_2H_4 + CO \qquad (2a)$$

$$CH_2 + H_2 \longrightarrow CH_3 + H \qquad (3a)$$

$$H + CH_2CO \longrightarrow CH_3 + CO \qquad (4a)$$

$$CH_3 + CH_3 \longrightarrow C_2H_6 \qquad (5a)$$

$$CH_3 + H_2 \longrightarrow CH_4 + H \qquad (6a)$$

$$CH_3 + CH_2CO \longrightarrow CH_2COCH_3 \qquad (7)$$

$$CH_3 + CH_2COCH_3 \longrightarrow C_2H_5COCH_3 \qquad (8)$$

Chanmugam and Burton objected[3] that they did not observe the formation of ethane-d_1 in ketene–deuterium–hydrogen photolyses. They thus argued against a process involving methyl radicals exclusively.

In a similar state of flux is the evidence concerning the mechanism of the reaction of methylene with methane. Grard and Vanpée[4] photolyzed ketene in the presence of methane and found carbon monoxide, ethylene and ethane as the major products of the reaction. They proposed the mechanism

$$CH_2CO + h\nu \longrightarrow CH_2 + CO \qquad (1a)$$

$$CH_2 + CH_2CO \longrightarrow C_2H_4 + CO \qquad (2a)$$

$$CH_2 + CH_4 \rightleftarrows C_2H_6 \qquad (13a)$$

Reaction 13a was thought to go to an excited ethane which is either stabilized by collision or dissociates to give methylene and methane. A reaction to give methyl radicals was ruled out as too endothermic. C and B used methane-d_4 and concluded that reaction 13a does not occur.

A better understanding of the mechanisms of these methylene reactions would facilitate the determination of the energies of consecutive dissociation of the bonds in methane

---

[1] J. Chanmugam and M. Burton, *J. Am. Chem. Soc.*, **78**, 509 (1956).

[2] H. Gesser and E. W. R. Steacie, *Can. J. Chem.*, **34**, 113 (1956).

[3] J. Chanmugam and M. Burton, *ibid.*, **34**, 1021 (1956).

[4] F. Grard and M. Vanpée, *Bull. Soc. Chim. Belge*, **60**, 208 (1951).

$$CH_4 \longrightarrow CH_3 + H \qquad D(CH_3\text{–}H)$$
$$CH_3 \longrightarrow CH_2 + H \qquad D(CH_2\text{–}H)$$
$$CH_2 \longrightarrow CH + H \qquad D(CH\text{–}H)$$
$$CH \longrightarrow C(g) + H \qquad D(C\text{–}H)$$
$$C(s) \longrightarrow C(g) \qquad L(C)$$

Most of the thermochemical values necessary to calculate the dissociation energies are known: $D(CH_3\text{–}H) = 102$, $D(C\text{–}H) = 82.7$, $L(C) = 171.7$, $\Delta H_f^0(H) = 52.1$, $\Delta H_f^0(CH) = 142.1$, $\Delta H_f^0(CH_4) = -17.9$, and $\Delta H_f^0(CH_3) = 32.0$ kcal./mole.[5,6] Since $D(CH_2\text{–}H)$, $D(CH\text{–}H)$ and $\Delta H_f^0(CH_2)$ are unknown, we are left with two equations in three unknowns. Mass spectrometric study of the appearance potentials of various ions in the mass spectra of methane, methyl and methylene has been used to solve this problem.[7–10] The ionization potential of methylene obtained by most workers using this method is 11.9 ev. Herzberg has now discovered a Rydberg series in the vacuum ultraviolet spectrum of methylene (triplet state) which converges to give an ionization potential of 10.4 ev.[11] This result casts grave doubt on the interpretation of the appearance potential data.

The data of Langer, Hipple and Stevenson[8] ($\Delta H_f^0(CH_2) = 66.4$ kcal./mole) yields a heat of reaction for (3a) of + 17.7 kcal. This endothermic value is not consistent with the conclusion of G and S that this reaction has a very low activation energy. Herzberg[11] observes the methyl spectrum and never the methylene spectrum when he photolyzes diazomethane in the presence of hydrogen. This is another indication that the reaction forming methyl radicals is exceedingly rapid and, therefore, is not endothermic.

$\Delta H_f^0(CH_2) = 82 \pm 8$ kcal./mole recently has been measured by observing the equilibrium concentration of methylene over hot carbon in an atmosphere of hydrogen.[12] This value makes reaction 3a almost thermoneutral.

The work reported in this paper was undertaken in an effort to resolve the unsettled questions concerning the reaction of methylene with hydrogen and methane and to shed some light on the question of the bond energies of methane.

Experimental

Diazomethane was produced in small quantities daily by the action of a saturated solution of KOH in ethylene glycol on N-methyl-N-nitroso-*p*-toluenesulfonamide (Eastman Kodak Co.).[13] The product was passed through a trap at −95° and then into a trap cooled in liquid nitrogen. Aliquots of the diazomethane were then distilled from this trap at −95° into small sample tubes cooled in liquid nitrogen, enough being collected in each tube for one run. These were kept frozen until the product was used. With this procedure no explosions ever occurred. The product was inferred to be pure from its mode of synthesis which yields no other gaseous products,[13] from its sharp transition from solid to liquid when warmed and from the reproducibility of vapor pressure measurements. The vapor pressures at −78, −86 and −95° are approximately 8.5, 2.5 and 0.65 mm., respectively. A Clapeyron–Clausius plot of the data yields a heat of vaporization of 10.5 kcal./mole (probably too high).

Hydrogen (Air Reduction Co.) was purified over uranium; mass spectrometric analysis showed it to be 99.98% pure. The hydrogen deuteride was prepared by passing D_2O through a tube packed with $LiAlH_4$.[14] The product was passed through two liquid nitrogen traps. Mass spectrometric analysis showed the final product to be 99.9% pure in hydrogen species with the isotopic composition, $H_2 = 0.02_7$, $HD = 0.95_2$ and $D_2 = 0.02_1$. The deuterium (General Dynamics Corp.) was analyzed as 99.95% pure in hydrogen species and 99.5% in deuterium. The remainder was hydrogen deuteride. Methane-d_4 (Merck and Co., Ltd.) was reported to be 99 atom % pure. Mass spectrometric analysis indicated that about 3% methane-d_3 was present. Helium (Matheson Co.) was purified by passing it through a tube filled with titanium sponge heated to 1150°. The ketene used in a few experiments was obtained from Mr. Delano Chong in this Laboratory, who prepared it from acetic anhydride by the method of Jenkins.[15] The product was twice distilled from traps at Dry Ice–trichloroethylene temperature and was stored at liquid nitrogen temperature.

All manipulations were performed in a conventional high vacuum system. The reaction system was a circulating flow system constructed entirely of Pyrex. The gases were circulated by an all-glass displacement pump driven electromagnetically from outside the system. The zone where the photolysis took place was enclosed in a water jacket for temperature control. The temperature of the water jacket was controlled to ± 2°. At either side of the irradiated zone were cold traps. During a run the upstream trap, containing diazomethane, was held at a temperature which provided the desired vapor pressure of diazomethane in the reaction zone. The downstream or product-collecting trap was cooled in liquid nitrogen, or in liquid oxygen for the runs with methane-d_4. The rate of circulation of gases in the reaction system was calculated from the characteristics of the pump. The calculations were tested by noting the time required to transfer all of a known quantity of diazomethane from the upstream to the downstream trap in a flow of hydrogen. The experimental and calculated pumping speeds agreed within a factor of two for the diazomethane pressures used under the assumption that equilibrium was established between the condensed and vapor phases. The circulation rate was such that the residence time of the gases in the irradiated zone was about one second. Diazomethane was admitted to the reaction system as a vapor at 10–15 mm., and this entire amount was frozen into the delivery trap with liquid nitrogen. The other reactants and inert gases were then admitted from a gas buret and the circulating pump was started. The product-collecting trap was cooled in liquid nitrogen and the delivery trap warmed to the appropriate temperature. The lamp, a General Electric A-H6 high pressure mercury arc, was then turned on. At the end of the run the upstream trap was warmed to room temperature and the product-collecting trap was warmed to −78°. The gases in the system were transferred by a Toepler pump into the gas buret, measured and then forced into sample bulbs. In some cases the product-collecting trap was warmed to room temperature and a second sample taken. This gas mixture was too complex to yield much information.

The analyses were done gas chromatographically with a Perkin–Elmer Model 154 Vapor Fractometer with Flame Ionization Detector. A silica gel column was used to separate methane, ethane and ethylene and a polypropylene glycol column for an estimate of the amount of higher hydrocarbons formed. The detector could be by-passed to

---

[5] H. G. Anderson, G. B. Kistiakowsky and E. R. Van Artsdalen, *J. Chem. Phys.*, **10**, 305 (1942).

[6] Selected Values of Thermodynamic Properties, National Bureau of Standards Circular 500.

[7] F. P. Lossing, K. U. Ingold and I. H. S. Henderson, *J. Chem. Phys.*, **22**, 621 (1954); F. P. Lossing, *Ann. N. Y. Acad. Sci.*, **67**, 499 (1957).

[8] A. Langer, J. A. Hipple and D. P. Stevenson, *J. Chem. Phys.*, **22**, 1836 (1954).

[9] R. I. Reed and W. Snedden, *Trans. Faraday Soc.*, **55**, 876 (1959).

[10] E. W. C. Clark and C. A. McDowell, *Proc. Chem. Soc.* (London), 69 (1960).

[11] G. Herzberg, *Proc. Roy. Soc.* (London), **A262**, 291 (1961).

[12] W. A. Chupka, D. J. Meschi and J. Berkowitz, paper presented at the Symposium on Chemical and Thermodynamic Properties at High Temperatures in connection with the XVIIIth International Congress of Pure and Applied Chemistry, Montreal, Canada, August 1961.

[13] T. J. DeBoer and H. J. Backer, *Rec. trav. chim.*, **73**, 229 (1954); **73**, 582 (1954).

[14] A. Fookson, P. Pomerantz and E. H. Rich, *J. Res. Natl. Bureau Standards*, **47**, 31 (1951).

[15] A. D. Jenkins, *J. Chem. Soc.*, 2563 (1952).

TABLE I

DEUTERIOETHANES FROM THE REACTION OF METHYLENE WITH HYDROGEN DEUTERIDE

$(HD)_0$, mm.	Final P, mm.	Composition of product ethane as percentage of total C_2H_6	C_2H_5D	$C_2H_4D_2$	$C_2H_3D_3$
47.4	64.6	32.6	48.5	18.5	0.3
47.8	79.8	23.2	50.5	26.3	[a]
51.2	149.7	28.2	46.4	25.4	0.1
53.4	72.7	26.6	49.1	23.8	.4
53.7	81.3	30.8	48.8	19.9	.4
91.7	128.6	13.1	51.0	36.0	[a]

[a] Product not detectable.

TABLE II

ISOTOPIC COMPOSITION OF RESIDUAL HYDROGEN DEUTERIDE

$\frac{\text{Final } P}{\text{Initial } P}$	$(H_2/HD) \times 100$	$(D_2/HD) \times 100$
Initial	2.73	2.07
1.05	2.77	1.93
1.14	2.78	2.16
1.25	2.83	2.05
1.36	2.81	2.05
1.40	2.92	2.03
1.67	2.98	2.10

collect effluent in a removable trap cooled in liquid nitrogen. Samples collected in this way were used for mass spectrometric analyses which were performed on a Consolidated 21–103 mass spectrometer using 70-volt ionizing electrons and electrostatic scanning. For analysis of the deuterioethane mixtures the instrument was calibrated with samples of the pure deuterioethanes obtained from Merck and Co. Ltd. The mass spectrometric breakdown patterns for these compounds are given in Appendix A.

Results

Hydrogen Deuteride.—The isotopic composition of the ethanes from the reaction of methylene with hydrogen deuteride is given in Table I. The second column gives the total pressure of the gases collected at the end of the run. This includes unreacted hydrogen deuteride, the hydrocarbon products and the nitrogen formed when the diazomethane decomposes. The increase over the initial pressure of hydrogen deuteride is due to photolysis of diazomethane which does not appear in the initial pressure measurement.

In calculating the isotopic ethane ratio from the mass spectrometric data, it makes little difference which of the ethane-d_2 isomers is assumed to be present, because this calculation is insensitive to the choice. The observed mass spectrum in the mass 24–29 region is dependent on this choice, however. Although 1,2-ethane-d_2 is the more abundant of the two isomers present, better agreement in the mass 24–29 region is obtained by assuming about 20% of the ethane-d_2 is the 1,1-isomer.

For a number of runs the residual hydrogen deuteride was examined mass spectrometrically to discover whether any change in isotopic composition had occurred. The results of these measurements are given in Table II. The ethylene fraction from one run was collected and analyzed mass spectrometrically also. Less than 3% of the ethylene contained deuterium.

Deuterium.—The isotopic composition of the ethanes from the reaction of methylene with deuterium is given in Table III. The breakdown patterns used for calculation of the compositions were for 1,1,2,2-ethane-d_4, 1,1,2-ethane-d_3 and the mean of the patterns for 1,1- and 1,2-ethane-d_2. Ethane-d_6 was not detected as a product of this reaction. In these mixtures 0.1% ethane-d_6 would have been detectable. Also included in column 6 of the table are the results of a few analyses of the residual deuterium from these runs. The diazomethane pressures indicated in this table and others in this paper are the vapor pressures of diazomethane over the liquid at the temperature of the delivery trap during the run. The ethylene fraction from two runs was analyzed and found to contain less than 7% deuterium.

TABLE III

DEUTERIOETHANES FROM THE REACTION OF METHYLENE WITH DEUTERIUM

P_{D_2}, mm.	$P_{CH_2N_2}$, mm.	P_{He}, mm.	Irradiation time, sec.	Temp., °C.	Final $\frac{[HD]}{[D_2]} \times 10^2$	Ethanes as percentages of total ethane fraction $-d_0$	$-d_1$	$-d_2$	$-d_3$	$-d_4$	$-d_5$
					0.49 (initial)						
45.2	8.5		300	100[a]	.49	12.5	23.7	39.8	17.4	6.5	0.2
43.3	8.5		480	100[a]	.51	11.4	24.8	40.2	17.2	6.5	..
41.8	8.5		300	100[a]		0.7	27.5	43.8	20.4	7.6	..
58.6	8.5		360	100[a]	.48	7.7	25.0	41.6	18.5	6.7	.5
106.8	2.5	250[b]	720	100[a]	.45	12.7	31.4	34.2	16.1	5.6	..
118.8	0.65	217.2	900	3.5		7.1	31.3	36.4	18.6	6.4	.3
99.2	.65	296.8	1080	3.5		9.4	28.7	36.7	18.5	6.6	..
112.9	.65	254.1	900	3.5		10.9	29.0	35.0	18.2	6.6	.1
94.5	.65		900	3.5		7.8	29.1	36.0	20.0	7.0	.2

[a] This temperature is an estimate, because the reaction system had no water jacket for these runs. [b] The inert gas in this run was nitrogen rather than helium.

The results of analyses for the average rate of formation of methane, ethane and ethylene are given in Table IV for the reaction at 3.5, 27, 60, and 76°. Also given are the results of the few photolyses of ketene–deuterium mixtures. The columns are labeled R_{CH_4}, $R_{C_2H_6}$, and $R_{C_2H_4}$, but they refer to the total rate of production of all the isotopic species.

Higher hydrocarbons were also formed in the reactions of methylene with the hydrogen isotopes. The total of the C_3, C_4 and C_5 hydrocarbons was less than 10% of the ethane and ethylene formed. The major portion of these higher products was saturated. Mass spectrometric analysis indicated deuteration of these products, but they were present

TABLE IV

PRODUCT YIELDS FROM THE DIAZOMETHANE–DEUTERIUM PHOTOLYSES

P_{D_2}, mm.	$P_{CH_2N_2}$, mm.	P_{He}, mm.	Irradiation time, sec.	R_{CH_4}[a] $\times 10^{-10}$	$R_{C_2H_6}$[a] $\times 10^{-12}$	$R_{C_2H_4}$[a] $\times 10^{-11}$	$r^b \times 10^{15}$
At 3.5°							
94.5	0.6_5		900	34.5[c]	15.22	22.4	26.8
112.6	$.6_5$		1000	11.9	5.13	10.3	13.35
157.1	$.6_5$		1000	8.62	3.91	55.4	7.95
210	$.6_5$		1000	11.8	5.61	60.0	6.89
269	$.6_5$		1000	4.22	3.21	8.69	2.48
306	$.6_5$		1000	4.59	2.90	32.2	2.53
366	$.6_5$		1000	3.44	3.30	8.31	1.49
100.7	2.5	182.3	900	51.9	7.43	28.5	54.2
102.4	2.5	43.6	900	72.5	13.49	118.2	55.1
108.2	2.5	140.8	900	42.2	7.32	26.4	41.1
131.5	2.5	55.5	900	61.2	14.45	36.4	35.0
107.3	2.5	148.7	960	51.3	10.44		42.3
94.9	2.5	148.1	900	72.3	13.03	43.0	60.3
At 27°							
93.2	0.6_5		1000	6.56	1.08	93.4	21.00
115.2	$.6_5$		1000	7.62	1.46	18.9	17.03
118.8	$.6_5$		1000	8.20	1.78	75.1	16.05
145.0	$.6_5$		1000	4.93	1.65	5.91	8.21
168.8	$.6_5$		1000	4.53	1.67	3.97	6.46
199	$.6_5$		1000	4.62	1.30	40.5	6.33
209	$.6_5$		1000	2.60	1.40	5.41	3.26
276	$.6_5$		1000	2.33	1.43	3.29	2.19
87.0	2.5		555	76.4	6.45	195.0	107.2
92.2	8.5	170.8	500	240.5	8.05	89.9	286.0
96.2	8.5	260.3	540	227.0	7.64	83.7	265.0
110.5	8.5		420	272.0	15.05	87.8	197.0
170	8.5		420	221.7	16.70	118.0	99.00
235	8.5		540	189.8	17.31	159.6	60.00
298	8.5		540	108.7	14.57	66.4	29.66
347	8.5		540	116.5	17.41	49.5	25.19
443	8.5		600	57.9	12.40	31.6	11.52
83.0	0.6_5[d]		1000	1.60	0.0014	16.3	
83.0	$.6_5$[d]		1000	1.11	0.0019	10.0	
83.0	$.6_5$[d]	229	1000	1.81	0.00014	38.8	
The ketene–deuterium reaction							
At 27°							
	P_{CH_2CO}						
126	12.5		1000	9.19	5.44	31.4	9.71
252	12.5		1000	8.38	4.07	15.5	5.12
120	12.5[d]		1000	6.92	0.0069	5.85	
At 60°							
81.2	0.6_5		1000	8.50	3.01	7.04	20.8
119.1	$.6_5$		1000	7.52	2.84	98.8	12.91
122.2	$.6_5$		870	11.4	4.22	55.5	15.9
160.9	$.6_5$		900	9.77	4.57	9.92	9.93
223.6	$.6_5$		960	7.51	4.00	8.97	5.63
262	$.6_5$		1000	3.03	1.91	5.46	2.89
272	$.6_5$		1000	3.74	1.82	39.2	3.51
331	$.6_5$		1000	4.78	1.82	40.6	3.69
At 76°							
133.6	0.6_5		1000	7.80	1.65	80.1	16.41
232	$.6_5$		1000	3.43	1.33	5.15	4.63
320	$.6_5$		1000	4.44	1.38	8.86	4.27
397	$.6_5$		1000	3.66	1.24	4.42	3.00
418	$.6_5$		1500	3.79	1.38	4.75	2.79

[a] The columns labeled R_{CH_4}, $R_{C_2H_6}$ and $R_{C_2H_4}$ refer to the total rate of production of all the isotopic species. Units are molecules/cc. sec. [b] The units are (cc./sec. molecules)$^{1/2}$. [c] Analysis for this run is unreliable. [d] For these runs 1.5 to 2 mm. of oxygen was added to the reaction mixture.

in quantities inadequate to determine the extent of deuterium substitution.

Hydrogen.—In order to make certain that any effects observed in the reaction of methylene with deuterium were not caused by some unknown isotope effect, a number of photolyses of diazomethane–hydrogen mixtures were carried out. The data obtained from these runs are given in Table V.

TABLE V

PRODUCT YIELDS FROM THE DIAZOMETHANE–HYDROGEN PHOTOLYSES

P_{H_2}, mm.	$P_{CH_2N_2}$, mm.	Irradiation time, sec.	R_{CH_4}[a] $\times 10^{-10}$	$R_{C_2H_6}$[a] $\times 10^{-12}$	$R_{C_2H_4}$[a] $\times 10^{-11}$	$r^b \times 10^{15}$
At 27°						
77.5	0.6_5	1000	14.88	6.88	72.1	22.74
104.5	$.6_5$	1000	8.90	4.67	80.5	12 21
130.5	$.6_5$	1000	7.38	4.14	8.26	8.62
151.0	$.6_5$	1000	7.34	4.12	60.1	7.42
179.5	$.6_5$	1000	6.70	3.75	28.5	5.89
263.5	$.6_5$	1000	7.37	4.74	10.0	3.99
337.5	$.6_5$	1000	7.25	4.14	16.33	3.28
421.5	$.6_5$	1000	7.38	3.90	10.1	2.75
492.5	$.6_5$	1000	6.98	3.32	7.88	2.42
At 68°						
136.5	0.6_5	1000	7.82	3.20	37.3	11.31
189.2	$.6_5$	1000	10.5	3.74	48.6	10.13
254.5	$.6_5$	1000	9.18	2.32	16.5	8.35
303.5	$.6_5$	1000	8.94	1.92	6.61	7.52
319.5	$.6_5$	1000	10.46	2.84	11.2	6.86
399.5	$.6_5$	1000	13.11	3.02	7.66	6.69

[a] The units are molecules/cc. sec. [b] The units are (cc./sec. molecules)$^{1/2}$.

Methane-d_4.—The vapor pressure of methane at liquid oxygen temperature is about 80 mm., so no pressures of methane-d_4 higher than this were used. Helium was used as an inert gas to extend the pressure range of these experiments. The runs were all carried out at 27° with the diazomethane delivery trap at −95°, giving a pressure of 0.6_5 mm. of diazomethane in the reactor. Irradiation time was 1000 seconds. The isotopic composition of the product ethanes is given in Table VI. The breakdown patterns chosen to calculate the compositions were 1,1,1,2-ethane-d_4, 1,1,1-ethane-d_3 and 1,2-ethane-d_2. The absolute concentrations of ethane in the product gases are not very meaningful. For the last two experiments recorded in Table VI the absolute values of the

TABLE VI

DEUTERIOETHANES FROM THE REACTION OF DIAZOMETHANE WITH METHANE-d_4

$[CD_4]_0$, mm.	$[He]_0$, mm.	Ethanes as percentages of total ethane fraction d_0	d_1	d_2	d_3	d_4	d_5	d_6
30.7		16.0	25.3	5.1	16.5	29.6	0.3	7.3
45.7		11.5	21.0	6.0	11.2	44.4	.2	4.7
57.0		..[a]	21.4	11.1	11.5	51.0	.1	4.9
62.9		8.6	15.8	5.1	9.9	56.1	.2	4.4
60.2	110.8	15.7	13.4	6.2	9.4	51.4	.4	3.6
66.7	138.1	..	6.1	6.2	..	85.9	..	1.9
62.5	211.0	..	2.7	10.6	..	85.2	..	1.5
64.7	291.8	1.6	10.3	5.0	3.2	77.6	.2	2.1
66.9	352.6	1.7	12.2	7.8	5.4	70.9	.2	1.9
70.4	399.6	3.2	12.5	6.6	5.3	70.0	.5	2.1
55.3[b]		..	..	6.2	..	92.4	..	1.5
53.4[b]	240.0	..	..	8.7	..	90.4	..	0.9

[a] The .. indicates product not detectable. [b] In these runs 1 to 1.5 mm. of oxygen was added to the reaction mixture.

ethane produced were compared and about the same amount of ethane was observed, $1.7 \pm 0.3 \times 10^{14}$ molecules/cc.

Mechanism of the Methylene–Hydrogen Reaction.—By analogy with the mechanism of G and S the following abstraction mechanism may be written for the production of ethane in the photolysis of diazomethane–hydrogen deuteride mixtures

$$\mathrm{CH_2N_2} + h\nu \longrightarrow \mathrm{CH_2} + \mathrm{N_2} \tag{1b}$$

$$\mathrm{CH_2} + \mathrm{CH_2N_2} \longrightarrow \mathrm{C_2H_4} + \mathrm{N_2} \tag{2b}$$

$$\mathrm{CH_2} + \mathrm{HD} \longrightarrow \mathrm{CH_3} + \mathrm{D} \tag{3b}$$

$$\mathrm{CH_2} + \mathrm{HD} \longrightarrow \mathrm{CH_2D} + \mathrm{H} \tag{3c}$$

$$\mathrm{H} + \mathrm{CH_2N_2} \longrightarrow \mathrm{CH_3} + \mathrm{N_2} \tag{4b}$$

$$\mathrm{D} + \mathrm{CH_2N_2} \longrightarrow \mathrm{CH_2D} + \mathrm{N_2} \tag{4c}$$

$$\mathrm{CH_3} + \mathrm{CH_3} \longrightarrow \mathrm{C_2H_6} \tag{5a}$$

$$\mathrm{CH_3} + \mathrm{CH_2D} \longrightarrow \mathrm{C_2H_5D} \tag{5b}$$

$$\mathrm{CH_2D} + \mathrm{CH_2D} \longrightarrow \mathrm{C_2H_4D_2} \tag{5c}$$

It is possible that reactions 3b and 3c are the net result of three reactions

$$\mathrm{CH_2} + \mathrm{HD} \longrightarrow \mathrm{CH_3D^*} \tag{3d}$$

$$\mathrm{CH_3D^*} \longrightarrow \mathrm{CH_3} + \mathrm{D} \tag{3e}$$

$$\mathrm{CH_3D^*} \longrightarrow \mathrm{CH_2D} + \mathrm{H} \tag{3f}$$

If so, the vibrationally excited methane might be collisionally deactivated to yield methane

$$\mathrm{CH_3D^*} + \mathrm{M} \longrightarrow \mathrm{CH_3D} + \mathrm{M} \tag{9}$$

The results of C and B indicating direct addition of methylene to hydrogen at lower temperatures might thus be reconciled with the mechanism of G and S.

The possibility that reaction 3d is a reversible reaction which could produce deuterated methylenes is ruled out on a number of grounds. This sort of scrambling would lead to formation of all the possible deuterioethanes and these are not observed. Moreover, this reaction would lead to isotopic mixing in the residual hydrogen deuteride and to the formation of ethylene containing deuterium. Little isotopic mixing is observed in the case of hydrogen deuteride (Table II) or in the reaction with deuterium (Table III) where the effect should be even easier to detect. The small degree of mixing observed probably is due to reactions of hydrogen and deuterium atoms.

The result of both the addition and the abstraction mechanism is formation of $\mathrm{CH_3}$ and $\mathrm{CH_2D}$. These lead by reaction 5 to ethane-d_0, ethane-d_1 and 1,2-ethane-d_2 which are observed as the products of the reaction. For a choice between the two mechanisms the results of deuterium experiments must be used.

In terms of the abstraction and addition mechanisms the deuterium reaction may be formulated as: Abstraction

$$\mathrm{CH_2} + \mathrm{D_2} \longrightarrow \mathrm{CH_2D} + \mathrm{D} \tag{3g}$$

$$\mathrm{D} + \mathrm{CH_2N_2} \longrightarrow \mathrm{CH_2D} + \mathrm{N_2} \tag{4c}$$

Addition:

$$\mathrm{CH_2} + \mathrm{D_2} \longrightarrow \mathrm{CH_2D_2^*} \tag{3h}$$

$$\mathrm{CH_2D_2^*} \longrightarrow \mathrm{CH_2D} + \mathrm{D} \tag{3i}$$

$$\mathrm{CH_2D_2^*} \longrightarrow \mathrm{CHD_2} + \mathrm{H} \tag{3j}$$

$$\mathrm{H} + \mathrm{CH_2N_2} \longrightarrow \mathrm{CH_3} + \mathrm{N_2} \tag{4b}$$

$$\mathrm{D} + \mathrm{CH_2N_2} \longrightarrow \mathrm{CH_2D} + \mathrm{N_2} \tag{4c}$$

For the abstraction reaction only 1,2-ethane-d_2 is expected as the product. The addition reaction mechanism predicts the formation of all the isotopic ethanes with zero through four deuteriums except 1,1,1-ethane-d_3 and 1,1,1,2-ethane-d_4. The observed isotopic composition of the product ethanes is in accord with the predictions of the addition mechanism. Although the formation of some methyl via the abstraction mechanism cannot be excluded, it is unnecessary to postulate the abstraction reaction as being of comparable rate with the addition reaction.

Neglecting isotope effects and the reaction of methyls with hydrogen to give methane, the concentration of $\mathrm{CH_3}$, $\mathrm{CH_2D}$ and $\mathrm{CHD_2}$ would be in the ratio 1:2:1. Association of these methyls to yield ethane would give ethane-d_0, d_1, d_2, d_3 and d_4 in the ratio 1:4:6:4:1. The data of Table III show that this ratio is approached but that more of the ethane with fewer deuteriums is formed than is predicted. Isotope effects based on the justifiable assumption that it is easier to lose a hydrogen atom than a deuterium atom from the excited methane molecule will not explain this observation, because they work to give larger amounts of the more highly deuterated species than predicted above. The results of the kinetic measurements for these reactions (see following section), together with the results of the photolyses of diazomethane–methane-d_4 mixtures, indicate that the over-all reaction is more complex than written above. Reactions of intermediates with diazomethane must be postulated and these reactions may introduce more hydrogen into the ethanes than predicted.

Final evidence proving the occurrence of the addition mechanism is furnished by the results of runs with added oxygen. The reaction of methylene with oxygen is slow whereas the reaction of methyl with oxygen is rapid.[16] Fast reactions of methylene ought to be little affected by the presence of oxygen, whereas the reactions of methyl observed in the absence of oxygen will be suppressed.[17] The addition of oxygen produces a dramatic reduction in the yield of ethane but has a much smaller effect on the methane and ethylene yields. Methane is still produced *via* the addition and stabilization reaction and ethylene by reaction of methylene with diazomethane. Ethane production, which is a result of methyl association, is almost entirely eliminated. These results show that the direct addition of methylene to hydrogen to yield methane does occur. Together with the results for the isotopic composition of the product ethanes, this is compelling evidence for the addition mechanism.

Kinetics of the Diazomethane–Hydrogen Photolysis.—The reaction sequence 1 through 6 written by G and S gives the following relationship between methane and ethane formation:

---

[16] (a) G. B. Kistiakowsky and K. Sauer, *J. Am. Chem. Soc.*, **78**, 5699 (1956); (b) B. S. Rabinovitch and D. S. Setser, *ibid.*, **83**, 750 (1961); (c) E. W. R. Steacie, "Atomic and Free Radical Reactions," American Chemical Society Monograph Series, Reinhold Publishing Corp., New York, N. Y., 1954.

[17] The oxygen pressure used was more than adequate to suppress completely the reaction of methyl radicals with hydrogen. Compare ref. 16c, Vol. II, pp. 527–537, with pp. 612–615.

$$r = \frac{R_{CH_4}}{R_{C_2H_6}{}^{1/2}[H_2]} = \frac{k_6}{k_5{}^{1/2}}$$

At any given temperature the value of r should be constant, independent of the concentrations of the reactants. The results obtained in this work (Tables IV and V) show a marked dependence of this quantity on the concentration of the reactants. The results indicate that r is inversely proportional to the square of the hydrogen species concentration and directly proportional to the diazomethane concentration. A plot of r as a function of $[CH_2N_2]/[D_2]^2$ for the results at 3.5° is given in Fig. 1. The plots for the other temperatures and for the hydrogen runs also give straight lines. The following reaction scheme formally explains the results for diazomethane–hydrogen photolysis

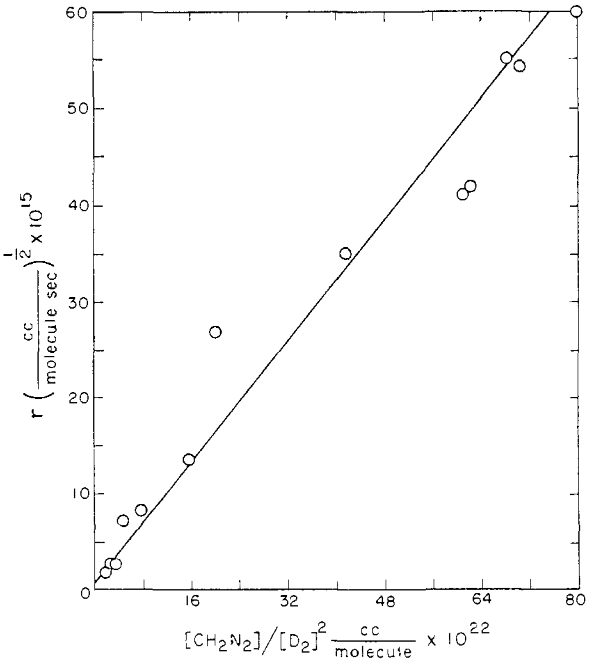

Fig. 1.—The variation of r with reactant concentrations for the diazomethane-deuterium runs at 3.5°.

$$CH_2N_2 + h\nu \longrightarrow CH_2 + N_2 \qquad (1b)$$
$$CH_2 + CH_2N_2 \longrightarrow C_2H_4 + N_2 \qquad (2b)$$
$$CH_2 + H_2 \longrightarrow CH_4{}^* \qquad (3k)$$
$$CH_4{}^* \longrightarrow CH_3 + H \qquad (3l)$$
$$CH_4{}^* + M \longrightarrow CH_4 + M \qquad (9)$$
$$H + CH_2N_2 \longrightarrow CH_3 + N_2 \qquad (4b)$$
$$CH_3 + CH_3 \longrightarrow C_2H_6 \qquad (5a)$$
$$CH_3 + CH_2N_2 \longrightarrow CH_3(CH_2N_2) \qquad (10)$$
$$CH_3(CH_2N_2) \longrightarrow CH_4 + CHN_2 \qquad (11)$$
$$CH_3(CH_2N_2) + H_2 \longrightarrow X \qquad (12)$$

Reaction 10 is analogous to the first step in the formation of methyl–ethyl ketone in the photolysis of ketene–hydrogen mixtures. Reaction 11 may be exothermic and require little activation energy. The free radical formed in this reaction could be quite stable, as the CHN_2 negative ion is stable enough to form salts.[18] In his flash spectroscopic studies with diazomethane Herzberg finds bands attributable to CHN_2.[19] The identity of the products of reaction 12 is unknown. One product might be ethane, thus explaining the presence of ethane with fewer deuteriums than predicted. Polymeric hydrocarbons and nitrogen-containing compounds could also be formed and would not be detected by the analytical techniques employed.

Neglecting the formation of methane *via* the quenching reaction 9 and assuming $k_{11}[H_2] > k_{10}$, the above reaction scheme gives the expression

$$r = \frac{k_6}{k_5{}^{1/2}} + \frac{k_{10}k_9}{k_5{}^{1/2}k_{11}} \frac{[CH_2N_2]}{[H_2]^2}$$

Qualitatively this equation predicts the correct dependence of r on the reactant concentrations. The intercept at infinite hydrogen concentration should be $k_6/k_5{}^{1/2}$. This rate constant ratio as a function of temperature is known.[20] For deuterium the ratio is 0.074, 0.38, 2.68 and 6.01 $\times 10^{-15}$ cc.$^{1/2}$ molecule$^{-1/2}$ sec.$^{-1/2}$ at 3.5, 27, 60 and 76°, respectively. For hydrogen the values are 3.09 and 24.5 at 27 and 68°. In all cases the intercepts obtained in this work were too low. This indicates, almost certainly, a second source of ethane in our reaction.

The addition of helium as an inert gas has no detectable effect on the reaction. It could only have an effect through reaction 9. Either reaction 9 may be such a minor source of methane under these conditions that the quenching effect is masked or helium may be very inefficient as a quencher for the excited methane. The results for the reaction of methylene and methane bear out the latter explanation.

The few experiments with ketene as the methylene source indicate that the reaction is not as complex as with diazomethane. The rate of formation of ethane in these runs is about the same as under comparable conditions with diazomethane, but the rate of production of methane is far lower. Hence, reactions analogous to (11) seem unimportant in the presence of ketene.

Mechanism of the Methylene-Methane Reaction.—A mechanism completely analogous to that for the methylene–hydrogen reaction may be written

$$CH_2N_2 + h\nu \longrightarrow CH_2 + N_2 \qquad (1b)$$
$$CH_2 + CH_2N_2 \longrightarrow C_2H_4 + N_2 \qquad (2b)$$
$$CH_2 + CD_4 \longrightarrow CH_2DCD_3{}^* \qquad (13b)$$
$$CH_2DCD_3{}^* + M \longrightarrow CH_2DCD_3 + M \qquad (14)$$
$$CH_2{}^*DCD_3{}^* \longrightarrow CH_2D + CD_3 \qquad (15)$$
$$CH_2D + CH_2D \longrightarrow CH_2DCH_2D \qquad (5c)$$
$$CH_2D + CD_3 \longrightarrow CH_2DCD_3 \qquad (5d)$$
$$CD_3 + CD_3 \longrightarrow C_2D_6 \qquad (5e)$$

If this relatively simple series of reactions were the whole story, the only ethanes observed would be 1,2-ethane-d_2, 1,1,1,2-ethane-d_4 and ethane-d_6. The data of Table VI indicate that some complicating side reaction yielding ethane with only a small amount of deuterium substitution is occurring. As in the case of the deuterium reaction, it is

---

[18] G. E. Maciel, MIT Seminar Abstracts, February 27, 1957.

[19] G. Herzberg, Address delivered before the XVIIIth International Congress of Pure and Applied Chemistry, Montreal, Canada, August, 1961.

[20] E. Whittle and E. W. R. Steacie, *J. Chem. Phys.*, **21**, 939 (1953).

probable that some ethane arises from diazomethane in an undetermined manner, but it is likely that the 1,1,1,2-ethane-d_4 and ethane-d_6 result only from the reactions written above. As would be expected, the formation of ethane-d_4 shows a dependence on the pressure. The scavenging effect of oxygen for methyls was again utilized to prove the direct addition and stabilization steps in the mechanism written. The formation of 1,1,1,2-ethane-d_4 almost exclusively in the presence of oxygen proves that direct addition occurs.

The above mechanism and the usual steady state assumptions about radical and excited intermediates lead to the following expression for the dependence of the yield of ethane-d_4 and ethane-d_6 on the concentration of quenching molecules

$$\frac{[C_2H_2D_4] - 2[C_2D_6]}{[C_2D_6]} = R = \frac{4k_{14}}{k_{15}}[M]$$

Figure 2 is a plot of R versus the pressure of methane-d_4 (M in the above expression) in mm. for the runs without added helium. The scatter is great, but a very rough estimate of the ratio k_{15}/k_{14} is possible. The value is 26 mm. and represents the pressure of methane-d_4 at which half the initially formed excited ethane-d_4 will dissociate to give two methyl radicals.

The side reactions of methyls should reduce the formation of ethane-d_6. The effect of this is to make the observed value of k_{15}/k_{14} probably a lower limit but correct to an order of magnitude.

The one square in Fig. 2 refers to a run with helium added to the reaction mixture. It is put on the graph at the coördinate corresponding to the methane concentration in this run. The position indicates that helium is a poor quencher, perhaps one-tenth as effective as methane. For the two reactions with added oxygen the methane-d_4 concentration was constant, but in one case helium was added. The amount of ethane formed in both runs, however, was the same within experimental error, showing again the very low quenching efficiency of helium.

Discussion

Reactions of Methylene.—We believe that the data presented are strong evidence for the addition as the first step in the reaction of methylene with hydrogen and methane. The addition results in the formation of vibrationally excited molecules. They are either stabilized by collision or break up unimolecularly to yield two radical fragments. The radical fragments go on to react with other species in the system or recombine.

The observation that ethane is one of the products of the reaction of methylene with hydrocarbons has been explained as an abstraction of a hydrogen atom by methylene to give methyls which associate to yield ethane.[21] The present results permit a different interpretation of this observation. Instead of abstraction, there is addition into the carbon–hydrogen bond to give an activated molecule with a methyl group at the addition site. If the molecule is not quenched by collisions, it may dissociate to give a methyl radical. The over-all result is the same as for direct abstraction, save that there should be an increasing tendency toward ethane formation as the pressure decreases. Indeed, this is the pressure effect which has been observed.[21]

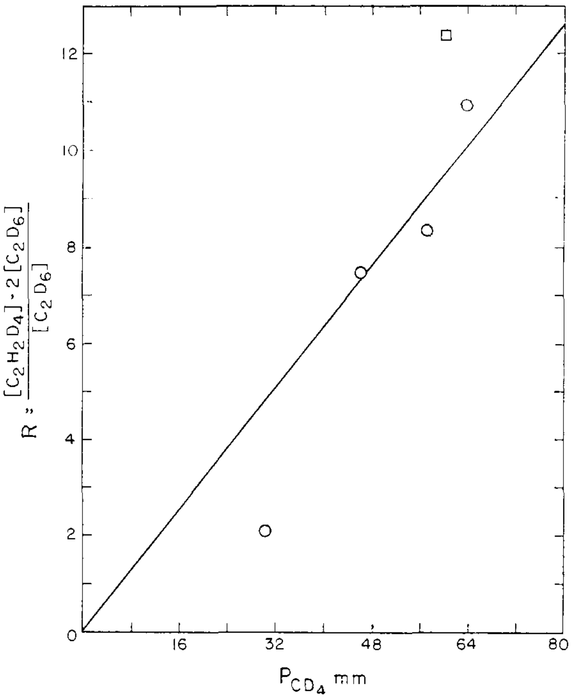

Fig. 2.—The pressure dependence of the deuterioethane ratio, R, in the methylene–methane-d_4 reaction: ○ no inert gas, □ helium added.

The results of Doering and Prinzbach[22] (on the addition of methylene at the 3-position in carbon-14-labeled 2-methylpropene-1) are explicable on the basis of the addition mechanism. In the liquid phase the addition will give an excited molecule which will almost immediately be deactivated by the frequent collisions it suffers. In the gas phase, however, the excited molecule will not be so rapidly quenched and will have a greater opportunity to decay to a methyl radical and a 2-methylpropenyl radical. Once the symmetric propenyl radical is formed recombination of methyl and propenyl will be equally probable at either end of the propenyl radical and isotopic mixing will occur as observed. If this explanation is correct, the amount of mixing should be pressure dependent. No data are presently available to test this hypothesis.

Although the results of C and B are completely at variance with the present results in many respects, their conclusion that the direct addition of methylene to hydrogen at room temperature occurs is confirmed. G and S obtain good kinetic results assuming a mechanism without direct addition, as a source of methane. They varied the pressure of hydrogen by about a factor of ten and might have been expected on the basis of the addition mechanism to observe a pressure effect on the formation of methane. Since, however, the present work indicates that helium is a poor

[21] H. M. Frey, *J. Am. Chem. Soc.*, **79**, 1259 (1957); **80**, 5005 (1958); *Proc. Roy Soc.* (London), **A250**, 409 (1959); *Trans. Faraday Soc.*, **57**, 951 (1961); *Proc. Chem. Soc.* (London), 318 (1959).

[22] W. von E. Doering and H. Prinzbach, *Tetrahedron*, **6**, 24 (1959).

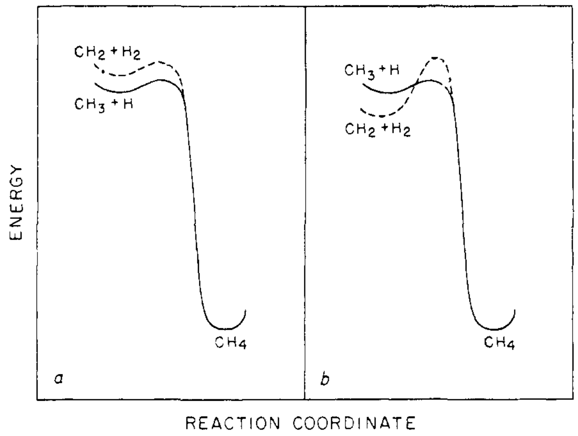

Fig. 3.—Possible reaction coördinate diagrams for the methylene–hydrogen molecule and methyl–hydrogen atom systems going to methane.

quenching molecule, hydrogen might also be expected to be inefficient and the pressure effect would be small. The methane yield would be dependent on the ketene concentration, but this was not varied greatly in their experiments. The loss of a small constant quantity of methane in the analyses could mask the pressure trend entirely. The possibility of such a loss is suggested in a recent article from Dr. Steacie's laboratory.[23] It is, thus, probable that the stabilization reaction was simply overlooked due to analytical difficulties in the G and S work.

The discrepancies between the present work and that of C and B appear principally in the isotopic analyses. At 27°, under the conditions of their experiments, they should have found ethane-d_4 as the principal deuterioethane in the reaction with methane-d_4. Instead, they found ethane-d_0 in ten-fold excess. The reaction with deuterium gave them only ethane-d_2. This is the major but not the exclusive deuterioethane formed in the present experiments with deuterium. The source of the differences between the present work and that of C and B is a mystery.

The Methane Bond Energies.—When it is first formed, the vibrationally excited methane from methyl and hydrogen necessarily has enough energy to reverse the formation step. That the reversal does not occur implies that the reaction which does occur is faster, presumably because of a lower energy requirement in the reaction coördinate. The reaction which does take place is the loss of a hydrogen atom to give a methyl radical. The minimum energy requirement for this reaction is 102 kcal. The minimum energy requirement for the reversal reaction must be $\geq$ 102 kcal. The over-all thermochemistry of these reactions may be combined as

$$\begin{array}{ll}
CH_4 \longrightarrow CH_2 + H_2 & \geq 102 \text{ kcal.} \\
CH_3 + H \longrightarrow CH_4 & -102 \\
H_2 \longrightarrow 2H & 104 \\
\hline
CH_3 \longrightarrow CH_2 + H & D(CH_2) - H)
\end{array}$$

Therefore, the second bond energy in methane is $\geq$ 104 kcal./mole. The reaction coördinate diagram for the processes considered would look like Fig. 3a.

It may be argued that the reaction $CH_2 + H_2 \rightarrow CH_4$ has a higher activation energy than the reaction $CH_3 + H \rightarrow CH_4$ but is fast because methylene is vibrationally and translationally "hot." Once the excited methane is formed the energy arguments with respect to competing unimolecular dissociations given in the preceding paragraph are the same, but the reaction coördinate diagram looks like Fig. 3b. Because the reaction of methylene with hydrogen is relatively slow (Table IV indicates that reaction with ketene is six times faster) and because of the ready loss of excess energy by methylene,[24] we reject this possibility and consider Fig. 3a to represent the true situation.

The value of the ratio of the rate constant for unimolecular dissociation of ethane formed from methylene and methane to the rate constant for collisional stabilization, $k_{\text{uni}}/k_{\text{col}} = k_{15}/k_{14} = 26$ mm., obtained in this work may be compared with the values given by Kistiakowsky and Roberts[25] for the methyl radical association reaction. The values given by them are for the reaction at higher temperatures. Because the large error in their values makes it difficult to say whether the ratio is temperature dependent, it will be assumed that it is not and the mean of their two values (3.6 mm.) used for comparison with the present value. The two sets of data will be compared using a formula derived from the unimolecular rate theory of Slater[26]

$$\frac{\tau_1}{\tau_2} = \left[\frac{E_2 - E_0}{E_1 - E_0}\left(\frac{E_1}{E_2}\right)\right]^{n-1}$$

The subscript 1 refers to the ethane formed from methane and methylene and 2 to the ethane formed by association of two methyls. $E_2 - E_0$ is estimated as 3 kcal./mole. E_0 may be approximated as the carbon–carbon bond energy in ethane, 84 kcal./mole. Assuming that the rate constant for collisional stabilization is the same for processes 1 and 2, the ratio of lifetimes is the inverse ratio of the rate constant ratios, $\tau_1/\tau_2 = 3.6/26$. If n is taken as 8,[27] substitution and solution gives $E_1 =$ 88 kcal. The over-all thermochemistry of the addition of methylene to methane may be written as

$$\begin{array}{ll}
CH_4 \longrightarrow CH_3 + H & D(CH_3\text{–}H) \\
CH_2 + H \longrightarrow CH_3 & -D(CH_2\text{–}H) \\
CH_3 + CH_3 \longrightarrow C_2H_6 & -E_2 \\
\hline
CH_2 + CH_4 \longrightarrow C_2H_6 & -E_1
\end{array}$$

Thermally equilibrated methylene and methane have almost the same thermal energy as two thermally equilibrated methyls so the contribution of thermal energy to E_1 is the same as to E_2. Then the combination of the other values gives $D(CH_2\text{–}H) = 103$ kcal./mole. Due to the many assumptions made, we set error limits of ±6 kcal./mole on this value.

---

[23] J. F. Henderson and E. W. R. Steacie, *Can. J. Chem.*, **38**, 2161 (1960).

[24] G. B. Kistiakowsky and K. Sauer, *J. Am. Chem. Soc.*, **80**, 1066 (1958).

[25] G. B. Kistiakowsky and E. K. Roberts, *J. Chem. Phys.*, **21**, 1637 (1953).

[26] N. B. Slater, "Theory of Unimolecular Reactions," Cornell University Press, Ithaca, N. Y., 1959.

[27] R. Gomer and G. B. Kistiakowsky, *J. Chem. Phys.*, **19**, 85 (1951).

TABLE VII

MASS SPECTRA OF THE DEUTERIOETHANES

m/e	C_2D_6[a]	C_2HD_5	$C_2H_2D_4$ 1,1,2,2	$C_2H_2D_4$ 1,1,1,2	$C_2H_3D_3$ 1,1,1	$C_2H_3D_3$ 1,1,2	$C_2H_4D_2$ 1,1	$C_2H_4D_2$ 1,2	C_2H_5D	C_2H_6
36	8.63	0.22								
35		8.65	0.20	0.20						
34	7.31	2.46	8.38	9.00	0.22	0.22				
33		6.31	4.37	4.28	9.49	8.81	0.16	0.28		
32	53.0	22.3	12.7	7.03	5.60	5.81	6.56	9.25	0.22	
31		30.0	26.5	33.5	8.92	18.6	5.50	7.55	10.1	0.26
30	15.7	9.85	22.0	20.0	40.9	29.3	17.1	27.6	8.60	10.9
29		6.25	9.43	9.70	13.5	16.5	23.5	25.6	36.1	9.93
28	12.9	8.89	8.43	8.43	9.82	9.74	20.0	14.2	23.2	46.6
27		2.65	5.11	5.05	7.45	7.08	14.1	9.60	12.3	17.1
26	2.18	1.83	2.05	1.99	2.85	2.77	10.1	4.50	7.37	12.2
25		0.20	0.45	0.45	0.79	0.75	2.26	1.16	1.68	2.48
24	0.42	0.36	0.38	0.37	0.41	0.39	0.77	0.45	0.47	0.51

[a] Carbon-13 peaks are eliminated in this pattern but may be obtained by adding 2.2% of the following even numbered mass peak height to each odd numbered mass peak height.

The two independent values of the second methane bond energy obtained here are in very good agreement, ≥104 and 103 ± 6 kcal./mole, respectively. These values are also in accord with the most recent spectroscopic and thermochemical findings.[11,12] All the results combined suggest the following energy "ladder" for the bond energies in methane

$$D(CH_3\text{–}H) = 102 \text{ kcal./mole}$$

$$D(CH_2\text{–}H) = 105 \pm 3$$

$$D(CH\text{–}H) = 108 \pm 3$$

$$D(C\text{–}H) = 82.7$$

Acknowledgments.—The authors wish to express their thanks to the National Science Foundation and to the California Research Corporation for grants which made this research possible. One of us (JAB) expresses his appreciation to the National Science Foundation for Fellowships held during the course of this research.

Appendix A

The mass spectrometric breakdown patterns for the deuterioethanes in the mass range 24–36 are given in Table VII since they may not all be found in the literature and may be of use to others. The breakdown patterns for all but two of the ethanes were given by Quinn and Mohler,[28] but there is a large discrepancy between their spectrum reported for 1,1,1-ethane-d_3 and the one we obtained. Lyon and Levy have used the results reported below with success.[29] A communication from Dr. Ausloos of the National Bureau of Standards indicates that the breakdown pattern has been redetermined and agrees with ours.[30] However, he indicates that the data presented here and by Quinn and Mohler for 1,1-ethane-d_2 are in error because the samples contain ethylene as a contaminant. Using Dr. Ausloos' new data the breakdown pattern for this ethane differs greatly from 1,2-ethane-d_2 only at those mass peaks corresponding to the loss of H_2, HD or D_2, which is consistent with the results for ethanes -d_3 and -d_4. The breakdown patterns presented have been normalized on the basis that the total number of ions produced in this region of the mass spectrum by each isotopic ethane is the same. The figures given are percentages of this total appearing at each mass number.

---

[28] E. I. Quinn and F. L. Mohler, *J. Res. Natl. Bureau Standards*, **65A**, 93 (1961).

[29] R. K. Lyon and D. Levy, *J. Am. Chem. Soc.*, **83**, 4290 (1961).

[30] P. Ausloos, private communication.

[CONTRIBUTION FROM THE ARGONNE NATIONAL LABORATORY, ARGONNE, ILLINOIS]

Consecutive Ion-molecule Reactions in Methane[1]

BY S. WEXLER AND N. JESSE

RECEIVED FEBRUARY 15, 1962

Reactions of positive ions with methane molecules have been studied at pressures of up to a few tenths of a millimeter in the source chamber of a mass spectrometer. Evidence indicates that increasingly heavy ions are formed in a chain of consecutive reactions between ions and the methane molecules. Some specific chains of such reactions are suggested. The two secondary ions CH_5^+ and $C_2H_5^+$ account for more than 70% of the total ion intensity at higher CH_4 concentrations. Cross sections for the reaction of primary ions with CH_4 have been determined from the exponential attenuations of the intensities of the individual species with increasing gas concentration. Reaction cross sections of the principal secondary ions have been estimated from the concentration dependences of the intensities of the secondaries. The resulting cross sections of the primaries agree reasonably well with those determined elsewhere by different methods. The results of the measurements are correlated with the ionic mechanism proposed for the reactions occurring in the radiolysis of CH_4.

A. Introduction

In the proposed mechanisms of chemical reactions occurring in the radiolysis of gases, it has usually been assumed that the primary ions produced by electron ionization and/or the secondary ions formed in the reactions of the primaries with the gas are neutralized by electron capture, and that the resulting free radicals then react to form

---

(1) Work performed under the auspices of the U. S. Atomic Energy Commission.