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The Tritium β-Ray Sensitized Exchange of Deuterium Atoms with Methane

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The exchange of deuterium atoms with methane in mixtures of TD, D_2, and traces of methane has been studied at temperatures from −196 to 225° at D_2 pressures near 1 atmosphere. CH_3D was the only exchange product detectable below 12% conversion, the more highly deuteriated methanes being formed as secondary products by exchange of CH_3D, CH_2D_2, etc. A chain mechanism was operative above 123° and proceeded with an apparent activation energy of about 16 kcal./mole. No evidence in support of H-atom abstraction was found, and a virtual absence of CH_3-radicals was indicated. Below 123° the exchange proceeded with an apparent activation energy of about 2 kcal./mole, presumably *via* an ion–molecule chain mechanism.

Introduction

The reactions of hydrogen atoms with methane have been a subject of investigation for many years. Steacie[4] has written a comprehensive and critical review of this work up to September 1953. The earliest investigators employed electrical discharge tubes to produce atomic hydrogen and consequently were obliged to work with flow systems at very low pressures. Despite serious experimental difficulties the discharge tube studies established that methane was surprisingly inert to attack by hydrogen atoms relative to ethane and higher hydrocarbons.[5-8] This relative inertness was attributed to a high energy of activation (12–18 kcal./mole) largely on the basis of collision yields calculated from data taken at a single temperature by assuming a normal steric factor of about 0.1. Later studies of the Hg-sensitized photolysis of D_2–CH_4 mixtures in static systems at high pressures and over a range of temperatures seemed to support this conclusion.[9,10] However, recent work[11] using a hot filament as a source of hydrogen atoms in a flow system and a very sensitive means for measuring the H-atom concentration in the presence and absence of methane indicates that the initiating step of the exchange reaction proceeds in this system at a very low activation energy (4.5 kcal./mole) requiring the assumption of an anomalously small steric factor of the order of 10^{-5}. It appeared to the present authors that reactions between D-atoms and methane might best be studied in a non-flow system at pressures of the order of 1 atm. using mass spectrometric analysis for direct determination of exchange products and gas chromotography for measurement of any simultaneous chemical changes. Contributions of surface-catalyzed reactions likely to occur in flow systems at pressures several orders of magnitude lower can clearly be minimized or eliminated, and certain control of the reaction temperature over a wide range is easily attained. Identification of isotopic and chemical products by direct methods of great sensitivity is also a clear advantage over indirect methods. Recent advances in the understanding of ion–molecule reactions indicate that hydrogen gas exposed to a constant intense source of ionizing radiation can provide an abundant and constant supply of hydrogen-atoms in a static system at high pressures.[12]

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[4] E. W. R. Steacie, "Atomic and Free Radical Reactions," 2nd Ed., Reinhold Publishing Corp., New York, N. Y., 1954.

[5] E. Boehm and K. F. Bonhoeffer, *Z. physik. Chem.*, **131**, 153 (1927).

[6] K. F. Bonhoeffer and P. Harteck, *ibid.*, **A139**, 64 (1928).

[7] H. V. Wartenberg and G. Schultze, *ibid.*, **B2**, 1 (1929).

[8] H. M. Chadwell and T. Titani, *J. Am. Chem. Soc.*, **55**, 1363 (1933).

[9] K. Morikaawa, W. S. Benedict and H. S. Taylor, *J. Chem. Phys.*, **5**, 212 (1937); *J. Am. Chem. Soc.*, **57**, 383 (1935).

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[11] M. J. Berlie and D. J. Le Roy, *Can. J. Chem.*, **32**, 650 (1954).

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Thus, provided that charge transfer and energy transfer reactions between methane and ionized and/or excited deuterium do not seriously interfere with or obscure atomic and free-radical reactions, a reaction system consisting of a large excess of D_2 undergoing radiolysis to form D-atoms in the presence of a trace of methane constitutes an excellent system for the study of homogeneous atomic and free-radical reactions under carefully controlled conditions. The overwhelmingly predominant reaction of D_2^+ is abstraction of a D-atom from deuterium in a single collision to form D_3^+[13–15] and the most likely fate of D_3^+ is neutralization, since D_3 has an ionization potential less than that of CH_4.[16] Thus, the 100-ev. yield of D-atoms will probably lie between 6 and 20, depending upon the products formed by neutralization of D_3^+ and the efficiency with which energy required/ion-pair in excess of the ionization potential leads to dissociation of deuterium molecules. Our results indicate that studies of reactions induced by tritium β-rays in gaseous mixtures of D_2, TD and traces of CH_4 provide valuable new insight into the kinetics of homogeneous gaseous reactions between hydrogen-atoms and methane with a degree of control over critical experimental conditions not previously attained.

Experimental

Deuterium gas (<99.5% D_2) obtained from the Stuart Oxygen Co., and from the General Dynamics Corp. was used without further purification. Carrier-free tritium gas was obtained from the Oak Ridge National Laboratory. Prior to each series of experimental runs measured amounts of deuterium and tritium were mixed and stored in a carefully outgassed 2-liter flask on a high vacuum system. The mixtures were protected from contact with stopcock grease during storage by a groundglass mercury float valve interposed between the storage flask and a stopcock to a manifold connecting with a conventional gas volume measuring section of the vacuum system. For each series of runs approx. 20 curies (7.7 cc. STP) of carrier-free tritium were diluted with deuterium to a total pressure of $^1/_4$ atm. to 1 atm. depending upon the desired dosage rate in reaction mixtures to be prepared. Each T_2–D_2 mixture was permitted to equilibrate and purge itself of traces of oxygen by self-radiolysis in the storage flask for several days before use. Phillips Petroleum Co. research grade methane (>99.68%) was further purified by distillation on a separate vacuum system through several liquid nitrogen traps, discarding about 90% of the starting material. The methane collected was stored on the vacuum system in an outgassed and evacuated 2-liter flask. Immediately before preparation of each reaction mixture (CH_4–D_2–TD) the small quantity of methane required was drawn from this flask and placed in contact with a freshly evaporated film of misch metal on the walls of a 500-ml. "getter" flask for several hours. Under the conditions employed such treatment is reported to reduce the oxygen content of methane–oxygen mixtures to less that 2.5 p.p.m.[17] and to effectively remove traces of unsaturated impurities.[18] Analysis by gas–solid partition chromatography using a hydrogen flame ionization detector indicated less than 5 p.p.m. of ethylene, approx. 2 parts/10,000 of ethane, and approx. 1 part/10,000 of propane in methane purified as described.

The reaction vessels were 500 cc. spherical Pyrex bulbs fitted with centered thermocouple wells. They were connected to the vacuum system through a 1 mm. capillary of about 15 cm. length and a capillary bore vacuum stopcock. Reaction temperatures at 25° and above were attained by enclosing the vessels within a circulating air bath. Control was maintained within ± 0.5° or better at temperatures up to 225° with a thermistor regulator and bridge circuit. Temperatures below 25° were obtained by immersing the vessels in suitable cooling mixtures. The reaction vessels were treated as follows before admission of reactants in order to minimize evolution of foreign gases from the vessel walls during experimental runs. Each vessel was pumped and baked at 510° in an electric furnace on the line for at least 12 hr. followed by 12 hr. at 440°. The all-glass vacuum system was maintained at pressures of the order of 10^{-6} mm. with a mercury diffusion pump backed by a conventional high-vacuum mechanical forepump.

Samples for analysis were taken periodically by opening the capillary stopcock to an evacuated section of tubing (4.65 cc.) between this stopcock and a 3-way stopcock directly above it. Each aliquot was transferred through this stopcock by means of a Toepler pump to a product gas measuring device where it was measured and pressed into a sample bulb through a greaseless 5/20 mercury cup joint. The relay of the automatic Toepler pump was triggered by changes in the capacitance of two copper coils occasioned by the rise and fall of the mercury, thus avoiding sparking within the sample gases and possible isotopic equilibration of the samples during transfer.

Measurements of the rate of energy deposition by tritium β-particles in the reaction mixtures were performed with a Cambridge Instrument Co. precision differential ionization chamber and quadrant electrometer. Suitably small measured aliquots of each mixture were admitted to the spherical 2-liter sample ion chamber, and both sample chamber and the identical reference chamber were filled to 1-atm. pressure with commercial dry nitrogen. Dosage rates were calculated from the measured saturation ion currents using a W-value for nitrogen of 34.9 ev./ion-pair and the finding that well over 99% of the tritium β-particles are absorbed in the gaseous contents of 500 cc. or larger spherical vessels at all pressures and in all gas mixtures used in this work.[19]

Mass spectrometric analyses were performed with a Consolidated Type 21–101 mass spectrometer. Analyses and calibration measurements for methane and the D-substituted methanes were performed using a 70 volt accelerating potential and an ionizing current of 50 μa. Pure samples of each of the four deuterated methanes were obtained from Merck and Co., Montreal. Analyses for protium, deuterium and protium deuteride were performed at 70 volts and a lower current of 10 μa. because of the great excess of deuterium over methane in each of the reaction mixtures. All experimental data reported are based on isotopic analyses at mass number 15 and greater because of the poor precision obtainable in analyses for protium deuteride in a great excess of deuterium at low exchange conversions.

Chemical analyses for hydrocarbon products were performed by gas–solid partition chromatography using a 2-meter silica gel column, helium carrier gas and a hydrogen flame ionization detector. Resolution for methane, ethane, ethylene and propane was excellent, and with the conditions employed (102°, 31 cc./min. flow rate), the instrument was able to detect on the order of 0.1 p.p.m. of each of the higher hydrocarbons in methane. The lower limits of detectability in each of the reaction mixtures were correspondingly greater in inverse proportion to the mole fraction of methane in these mixtures. Thus, in reaction mixtures containing 0.1 mole % methane, it was possible to detect 1 part/10,000 of ethane in methane of the mixture.

$G(CH_3D)$ (molecules of monodeuteriomethane formed/100 ev. absorbed by the entire reaction mixture) was calculated for each experimental run at constant temperature by means of the expression $G(CH_3D) = (dX_{CH_3D}/dt)\cdot(X_{CH_4}PA)/(10\ RTI)$, where X_{CH_3D} equals the number of moles of CH_3D divided by the total number of moles of all isotopic forms of methane in the sample at time t, P is the total pressure of the reaction mixture at temperature T

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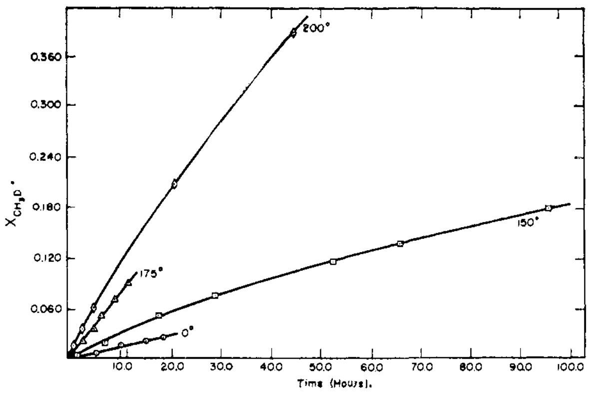

Fig. 1.—Representative plots of the mole fraction of CH_3D relative to all isotopic forms of methane *vs.* time at 0, 150, 175 and 200°.

prior to the beginning of the run, A is Avogadro's number, R is the gas constant, and I is the dosage rate (ev./cc. sec.). Values of dX_{CH_3D}/dt were measured from experimental plots of X_{CH_3D} *vs.* time. All such plots were found to be strictly linear within analytical uncertainty at conversions of methane to monodeuteriomethane less than about 5% at each of the constant temperatures from −196 to +228°. At higher conversions, the rate of CH_3D formation was observed to decrease, steadily approaching zero at about 50% exchange. All $G(CH_3D)$ values reported in Table I were measured at conversions of 5% or less, unless otherwise noted, and probably are equal within 5% to the initial 100-ev. yield at each of the temperatures reported. It is apparent that the total pressure of the system decreases by a constant factor $V_r/(V_r + V_s)$ with each sampling, where V_r is the volume of the reaction vessel and V_s is the volume of the sampling section (4.65 cc.). However, the dosage rate decreases in the same proportion with each sampling, and it can be shown easily that $G(CH_3D)$ for each constant temperature experiment is correctly represented by the expression written above.

Results and Discussion

Data reported in Table I refer to a series of experiments in which the initial rate of formation of deuterated methanes in gaseous mixtures of D_2, TD and CH_4 was measured at a series of constant temperatures from −196° to 225° in a static (non-flow) system at total pressures near 1 atmosphere. Figure 1 presents several representative plots of X_{CH_3D} (moles CH_3D/total moles of methane) *vs.* time and illustrates the linear relationship observed in all experimental runs carried to 5% exchange or less. It was also observed, as partially illustrated by Fig. 1, that the net rate of formation of CH_3D decreased gradually but perceptibly beyond about 5% exchange and rapidly approached zero at approximately 50% conversion (runs 1, 3 and 17). CH_3D was the only exchange product detectable at conversions of CH_4 less than about 12%; the initial rate of formation of CH_2D_2 was zero at all temperatures. Beyond 12% conversion CH_2D_2 was the only additional deuterated methane detected and was a minor exchange product in all cases up to at least 55% conversion. CHD_3 and CD_4 were not detected in any experiments; however, analyses were not performed on any samples beyond about 55% conversion.

As illustrated in Fig. 2, the initial 100-ev. yield of monodeuteriomethane, $G(CH_3D)$, increased steadily with increasing reaction temperature between −21 and 225°. A change of mechanism

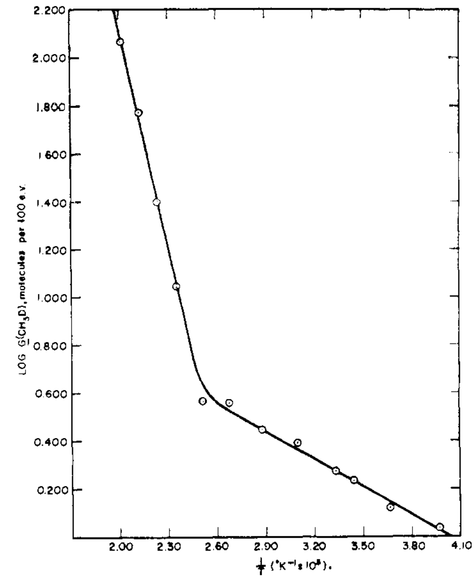

Fig. 2.—Temperature dependence of $G(CH_3D)$.

is indicated at about 120°. The apparent over-all energy of activation below 120° is 2.0 ± 0.2 kcal./mole and that between 120 and 225° is 14 ± 1 kcal./mole. The magnitude of $G(CH_3D)$ at the higher temperatures clearly indicates a chain mechanism for the exchange, since conservation of energy fixes the upper limit of the 100-ev. yield of D-atoms from the radiolysis of D_2 at about 20. Eyring, Hirschfelder and Taylor[20] estimate $G(H\cdot)$ from H_2 in the α-ray induced ortho-para conversion to be about 16, and Lind's interpretation of $G(-H_2)$ in the α-

TABLE I

Run no.	X_{CH_4}	Temp., (°C.)	$G(CH_3D)$	Dosage rate, ev./cc. STP-hr. × 10^{-16}
13	0.138	−196	0.0	2.80
16	.002	−196	7	3.14
20	.0163	−150	0.0[a]	3.09
18	.0163	− 78	7.6[b]	3.09
21	.0163	− 78	11.4[c]	3.09
22	.0163	− 21	1.08[d]	3.09
8	.0166	0	1.32	2.80
19	.0163	18	1.7[e]	3.09
9	.0166	27	1.88	3.20
10	.0166	50	2.46	3.20
6	.0146	75	2.3	2.80
7	.0558	75	2.8	2.68
14	.001	77	0.70	3.14
15	.002	77	0.85[f]	3.14
5	.0204	100	3.62	2.24
11	.0166	123	3.66	3.20
2	.0172	150	11.1	0.822
12	.138	152	11.2	2.80
17	.002	152	...[g]	3.14
4	.0115	175	25.1	1.03
1	.0163	200	59.9	0.823
3	.0161	225	117	0.824

[a] Measured between 17 and 19% conversion. [b] 7 to 11% conversion. [c] 23 to 26% conversion. [d] 27 to 29% conversion. [e] 12 to 16% conversion. [f] 16 to 22% conversion. [g] Carried from 46 to 55% conversion.

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(20) H. Eyring, J. O. Hirschfelder and H. S. Taylor, *J. Chem. Phys.*, **4**, 479 (1936).

ray induced synthesis of water-vapor[21] as the 100-ev. yield of H-atoms by considering O_2 as an efficient H-atom scavenger permits an estimate of $G(H\cdot)$ of about 20 atoms/100 ev.

No indications of sensitivity of exchange yields to modest variations in total pressure or in dosage rate were found at any temperature. Initial total pressures in each of the entire series of reaction mixtures were equal at their respective temperatures within ± 10% of 76 cm. Initial dosage rates, as reported in Table I, were varied by as much as a factor of 4 with no apparent systematic effect on the initial yields of CH_3D. It should be noted, however, that the lowest rates were employed at the highest temperatures and *vice versa* for practical reasons, since it was necessary even with the highest dosage rates to perform observations over periods of many hours for a single run.

It seems clear from the shape of the growth curves for CH_3D and from other evidence cited below, that the exchange rate is proportional to the CH_4 concentration. A zero order dependence on CH_4, such as one might observe in a typical radiolytic scavenger system with a great excess of efficient scavenger, is clearly not indicated; the yields are too small, and CH_4 is too inert to serve as an efficient scavenger for D-atoms. Several direct attempts to investigate the effect of the initial CH_4 concentration on the initial $G(CH_3D)$ were made (runs 6 and 7; 14 and 15; 2 and 12). In each case $G(CH_3D)$, initial, was greater with the larger initial CH_4 concentration. Unfortunately, an increase in the initial CH_4 concentration produces, among other effects difficult to assess at this time, a decrease in the D-atom concentration caused by absorption of a proportionally greater fraction of the tritum β-ray energy by CH_4. This is a particularly troublesome limitation in attempts to obtain a several-fold increase in the CH_4 mole fraction from a base value of 0.01 to 0.02, since the electron fraction of CH_4 is five times its mole fraction in dilute mixtures. An attempt was made to work in a concentration range one order of magnitude lower (runs 14 and 15), but it was unfortunately necessary to carry the total conversion in run 15 to 22% of the CH_4 originally present at 0.002 mole fraction. Comparison of runs 14 and 6 seems most significant and indicates a direct but apparently less than first order proportionality between the initial $G(CH_3D)$ and the initial CH_4 concentration at 75–77°. Several runs containing initial methane mole fractions of about $^1/_2$ were also performed at room temperature. In each, ethane, ethylene and propane were formed with G-values in good agreement with earlier reported values from the radiolysis of methane.[22] A 50:50 mixture of D_2 and CH_4 is, however, radically different from mixtures used for runs reported in Table I, since at least 83% of the β-ray energy will be absorbed directly by CH_4 in a 50:50 mixture, and charge transfer between D_2^+ and CH_4 probably competes quite effectively with the ion-molecule reaction of D_2^+ in a 50:50 mixture. More significantly, no ethane, ethylene or propane (beyond traces present initially) were detected at any time in runs 14, 15 and 17 which were performed with a single starting mixture at 77, 77, 152° and intermediate temperatures to a total conversion of 55% and a total dosage of approximately 5×10^{20} ev. This establishes the maximum possible rate of ethane formation at less than 10^8 molecules/cc. sec. $[G(C_2H_6) < 0.001]$.

In experiments performed at −78, −150 and −196°, an apparent inverse dependence of the exchange rate on methane concentration was observed (runs 13, 16, 18, 20). Inhibition of the exchange by CH_4 seems to be indicated at the lowest temperatures. At these temperatures the exchange must surely be effected *via* reactions of charged and excited species, possibly on a surface. Thus, inhibition by CH_4 may involve quenching of excited molecules (possibly self-quenching) by CH_4 or charge transfer from D_2^+ to CH_4 instead of the ion-molecule reaction $(D_2^+ + D_2 = D_3^+ + D\cdot)$ which has been observed to occur on every collision at much higher temperatures.[13–15] Additional work at very low temperatures and at higher temperatures and higher methane concentrations is planned for the near future.

Exchange Mechanism.—An atomic and free-radical mechanism for the β-ray sensitized exchange between D_2 and CH_4 may include several or all of the following formal reaction steps at low conversions

$$D_2 \overset{I}{\rightsquigarrow} 2D\cdot \qquad (1)$$

$$D\cdot + CH_4 \longrightarrow HD + CH_3\cdot \qquad (2)$$

$$D\cdot + CH_4 \longrightarrow CH_3D + H\cdot \qquad (3)$$

$$H\cdot + D_2 \longrightarrow HD + D\cdot \qquad (4)$$

$$CH_3\cdot + D_2 \longrightarrow CH_3D + D\cdot \qquad (5)$$

$$2CH_3\cdot \longrightarrow C_2H_6 \qquad (6)$$

$$2D\cdot \xrightarrow{D_2} D_2 \qquad (7)$$

$$H\cdot + D\cdot \xrightarrow{D_2} HD \qquad (8)$$

$$D\cdot \xrightarrow{D\text{-}S} D_2 \qquad (9)$$

$$H\cdot \xrightarrow{D\text{-}S} HD \qquad (9a)$$

$$CH_3\cdot \xrightarrow{D\text{-}S} CH_3D \qquad (10)$$

where I is the dosage rate (ev./cc.-sec.) and D–S represents a surface adsorbed D-atom whose concentration dependence may lead to either first or second order recombination at the walls. Every reasonable effort has been made to interpret our results in a manner consistent with Berlie and Le Roy's abstraction mechanism (reaction 2) and with their low value for E_2(4.5 kcal./mole).[11] There are, however, several important obstacles to an interpretation favoring either an abstraction mechanism for exchange, below about 123°, or a low value for thermal activation of the reaction of D-atoms with methane. Choosing reactions 1, 2, and first-order D-atom and CH_3-radical reactions *via* (9) and (10) for the range −21° to about 100°, one obtains by assuming a steady-state for D-atoms and for D–S species and that $(D\cdot) >> (CH_3\cdot)$,

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[21] S. C. Lind, "The Radiation Chemistry of Gases," ACS Monograph No. 151, Reinhold Publishing Corp., New York, N. Y., 1961; *J. Am. Chem. Soc.*, **41**, 531 (1919).

[22] F. W. Lampe, *ibid.*, **79**, 1055 (1957).

the rate law $G(CH_3D) = 200k_1k_2(CH_4)/[k_2(CH_4) + 2k_9]$. Assuming $G(D\cdot) = 16$, it follows that the ratio $k_2(CH_4)/2k_9$ varies from 0.06 to 0.2 between −21 and 75°, and the rate law assumes the limiting form, $G(CH_3D) = 100k_1k_2(CH_4)/k_9$ at the lower temperatures. If second-order recombination of D-atoms and CH_3-radical reaction with D-atoms at the walls are assumed, the rate equation becomes $G(CH_3D) = 100(k_1I/k_9)^{1/2}\, k_2(CH_4)$ at the lowest temperatures, and the low temperature limiting slope of Fig. 2 will again be a direct measure of E_2. In both cases the complete rate equations predict an Arrhenius plot which is concave toward the axes. Consideration of possible values for $G(D\cdot)$ indicates that this curvature should be distinctly apparent above room temperature. If 3-body homogeneous recombination for D-atoms and CH_3-radical reaction with D-atoms at the walls are assumed, it is possible to calculate hypothetical values for k_2 at each temperature from the data of Table I by means of the expression $k_2 = (14.2)[k_7(D_2)I]^{1/2}\, G(CH_3D)/(CH_4)\quad [G(D\cdot)\text{-}G(CH_3D)]^{1/2}$, which is valid at temperatures low enough to preclude the possibility of all D-atoms reacting with CH_4. The Arrhenius plot for k_2 so obtained leads to a maximum hypothetical value of about 2.5 kcal./mole for E_2 between −21 and 75°. The slope of this plot is quite insensitive to the choice of $G(D\cdot)$ and does not depend upon the value chosen for $k_9(6.7 \times 10^{-32}$ cc.^{2} sec.).[9] This hypothetical value for E_2 (≤ 2.5 kcal./mole) corresponds to a ΔH for reaction 2 of -8 ± 1 kcal./mole, using Steacies' best value for the activation energy of the reverse reaction.[4] The best available bond strengths from electron impact and thermal data clearly favor $\Delta H = -2 \pm 1$ kcal./mole.[23,24] This discrepancy appears sufficiently great to preclude the possibility that E_2 is as small as 2 to 3 kcal./mole, even allowing for a reasonable uncertainty in the relation $\Delta H = E_f - E_r$.[11]

Berlie and Le Roy observed the formation of ethane as evidence that CH_3- radicals were formed in their hot-wire, flow system experiments.[11] The absence of ethane as a product in our experiments suggests a virtual absence of CH_3-radicals in our experiments at the lowest mole fractions of CH_4. The rate of ethane formation in each of runs 13, 14 and 15 must have been less than 10^8 molecules/cc. sec., an upper limit corresponding to the maximum concentration which could reasonably have escaped detection (1 part of ethane in 10,000 parts of methane). With the abstraction mechanism, the rate of formation of CH_3-radicals equals $k_2(D\cdot)(CH_4)$, which is equal at 77° to 8.6×10^{11} radicals/cc. sec. This must also equal the rate of loss of CH_3-radicals to form CH_3D, since ethane formation was not observed. The most favorable possible choice of mechanism for formation of CH_3D, however improbable, is second-order homogeneous combination with D-atoms. Hence, $(CH_3) = (8.6 \times 10^{11})/[2k(D\cdot) + k_5(D_2)]$. The upper limit of a numerical value for the rate constant, k, is that for second-order (two-body) homogeneous combination of methyl radicals, a reaction with a steric factor of about unity and low or zero activation energy.[25] A most favorable estimate of the D-atom concentration for this purpose may be made using Berlie and Le Roy's low value of k_2. Thus, we compute a D-atom concentration of about 3×10^{11} atoms/cc. and $(CH_3\cdot) \geqslant 2 \times 10^{10}$ radicals/cc., using $k_5 = 1 \times 10^{-18}$ cc./molec. sec.[26] This provides a lower limit for the rate of ethane formation of about 2×10^{10} molecules/cc. sec, or about two orders of magnitude faster than the fastest rate which might have escaped detection. More reasonable estimates of the hypothetical CH_3-radical concentration based on less efficient reaction with D-atoms will lead to expected rates of ethane formation several orders of magnitude faster.

The possibility that k_2 is at least 100 times smaller than Berlie and Le Roy's value is sufficient to account for the absence of ethane, but this requires the assumption that E_2 is at least 3 to 4 kcal./mole greater than Berlie and Le Roy's value (4.5 kcal./mole) or that the steric factor is of the order of 10^{-7}. The most reasonable conclusion is that D-atoms did not enter into homogeneous gas phase reactions with methane below about 120°, although it is possible that they may have reacted at the walls in this system as well as in a low pressure flow system, as suggested by Harris.[27]

An argument against the occurrence of reaction 2 at any of the temperatures investigated may be based upon repeated observation that CH_3D was the only exchange product below 12% conversion [$G(CH_2D_2)$, initial, was zero] and that CHD_3 and CD_4 were undetectable up to at least 55% conversion. Others have observed distributions heavily favoring the more highly deuterated products in studies of reactions of D-atoms with methane,[28] ethane,[29,30] and propane[31] and have interpreted them as direct evidence for the presence of methyl radicals, which reportedly exchange much more readily with D-atoms than does methane.[9] Indeed, Coillet and Harris[28] have interpreted a preponderance of CHD_3(13%) and CD_4(80%) as strong evidence that the abstraction mechanism alone was operative in discharge tube experiments with methane at 340 to 370°.

It was anticipated that the certain presence of ionic species and a probable variety of uncharacterized excited species would probably lead to one or more reactions forming CH_3D and other possible products and that a constant low background contribution of these reactions might be observed independent of temperature. An interpretation of recent investigations of the self-induced exchange of tritium gas with methane suggests that reactions of the type, $CH_5^+ + T_2 = CH_4T^+ + HT$, may require 2 to 4 kcal./mole of activation

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energy.[32] It is interesting to postulate that the formation of CH_3D between −21 and 123° is caused by a chain of ion–molecule reactions, one or more of which requires a small thermal activation energy. A plausible ion–molecule chain mechanism is

$$D_2^+ + D_2 \longrightarrow D_3^+ + D\cdot \tag{11}$$

$$D_3^+ \xrightarrow{e^-} D_2 + D\cdot(\text{or } 3D\cdot) \tag{12}$$

$$D_3^+ + CH_4 \longrightarrow CH_4D^+ + D_2(\text{or } 2D\cdot) \tag{13}$$

$$CH_4^+ + D_2 \longrightarrow CH_4D^+ + D\cdot \tag{14}$$

$$CH_4D^+ + CH_4 \longrightarrow CH_5^+ + CH_3D \tag{15}$$

$$CH_5^+ + D_2 \longrightarrow CH_4D^+ + HD \tag{16}$$

$$CH_4D^+(\text{or } CH_5^+) + e^- \longrightarrow CH_3\cdot + HD \tag{17a}$$

$$\llcorner\!\longrightarrow CH_2 + HD + H\cdot \tag{17b}$$

$$CH_4D^+(\text{or } CH_5^+) + CH_4 \longrightarrow C_2H_x^+ + \text{other products} \tag{18}$$

Reaction 11 is well established.[13−15] Proton transfer reaction 13 is energetically favorable by about 53 kcal./mole on the basis of the proton affinities of D_2 and CH_4[33] and may compete relatively favorably with neutralization reaction 12 even at low methane concentrations. Reaction 14 has been reported by Frankevich and Tal'Roze,[34] although Lampe and Field[35] were unable to observe protonation of methane in either CD_4–H_2 or CH_4–D_2 mixtures in the mass spectrometer. It appears to be a reaction of relatively low cross section for an ion-molecule reaction but should proceed rapidly at D_2 pressures as high as 1 atm. Reactions 15 and 16 are plausible hydrogen-atom transfer reactions of a type frequently postulated.[33] Evidence for reactions 17a and 17b has been observed in the radiolysis of mixtures of methane, hydrogen and rare gases.[36] Reaction 18 is included as a possible chain-terminating step of necessarily low frequency. The rate constant for reaction 15 must be greater than that of reaction 16 by at least $(D_2)/(CH_4)$, or about 50, in order to account for the absence of the more highly deuterated methanes.

It appears, then, on the strength of several independent arguments, that reactions of atomic hydrogen with methane probably did not occur below about 123°. It also seems unlikely, for two reasons, that abstraction reaction 2 contributed to any great extent between 123 and 225°. First, all evidence indicates that CH_2D_2 was formed by D-atom reactions with CH_3D, and that CHD_3 and CD_4 were not formed prior to about 55% exchange. This is contrary to expectations, if CH_3-radicals were important chain carriers at the higher temperatures, for reasons cited above, and is also in sharp contrast to observations of the Hg-photosensitized exchange between D_2 and CH_4,[9] in which relatively large yields of CH_2D_2, CHD_3 and CD_4 were found in the same range of temperatures. Secondly, the apparent activation energy at the higher temperatures (14 kcal./mole) is too large to be assigned to reaction 2 unless an activation energy of about 16 kcal./mole can be assigned to the reaction, $CH_3\cdot + H_2 = CH_4 + H\cdot$. Experimental values as large as 16 kcal./mole have been observed, but available evidence seems to support a best value of about 10 kcal./mole.[4] There remains the possibility that above 123° every D-atom exchanged with methane, in which case the apparent activation energy (14 kcal./mole) could be interpreted as a measure of E_5, but this seems highly improbable in the light of evidence against the presence of CH_3-radicals in appreciable abundance. It is proposed, therefore, that, above 123°, CH_3D was formed predominantly *via* reaction 3 with a small contribution from the 2 kcal./mole process. The rate equation obtained by assuming a steady-state for H-atoms and first-order recombination at the walls is $G(CH_3D) = (200)k_1k_3k_4(D_2)(CH_4)/[2k_4k_9(D_2) + k_3k_{9a}(CH_4)]$. Now, $k_9 \simeq k_{9a}$, $(D_2)/(CH_4) \simeq 50$, and, assuming that all H-atoms reacted with D_2 *via* reaction 4, as is the case in the radiolysis of gaseous mixtures of H_2O and D_2 under nearly identical conditions,[37] the rate law assumes the form, $G(CH_3D) = (100)k_1k_3(CH_4)/k_9$. With second-order or 3-body homogeneous recombination, the rate law becomes $G(CH_3D) = (100)k_3[k_1/k_9(M)I]^{1/2}(CH_4)$, where (M) represents a third body or active surface. In any case, only k_3 will exhibit an appreciable temperature coefficient. Thus, E_3 has been estimated from the slope of a plot similar to Fig. 2 after subtraction of small extrapolated values for contributions of the 2 kcal./mole process. The activation energy for reaction 3 so obtained is 16.0 ± 1.5 kcal./mole.

This work lends support to early indications[5−8] that the relative inertness of methane toward hydrogen-atoms is a consequence of a high energy of activation rather than an extremely small steric factor. Theoretical considerations[38,39] appear to have demonstrated that a mechanism which requires inversion of the methane tetrahedron cannot occur with an activation energy less than about 37 kcal./mole. It must be concluded for the present that exchange occurred *via* a non-abstraction mechanism other than the inversion model of Gorin, *et al.*, possibly by means of a simple displacement of a hydrogen atom on the same side of the molecule as the attacking atom and with a line of approach other than along the line of centers of the C–H bond.

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