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The Reactions Between Atomic Deuterium and the Saturated Aliphatic Hydrocarbons

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The exchange reactions between atomic deuterium and methane, ethane, propane and butane have been studied in the range of temperatures, 0–300°C, in each case until significant amounts of exchange have been obtained. The extent of deuterization and the nature of the fragments produced have been examined by fractionation analysis and determination of the thermal conductivities of the fractions. From the temperatures at which the several interactions occur, approximate values for the activation energies of the individual processes have been deduced and these have been shown to conform with the mechanisms

of reaction formulated. It has been indicated that deuterization of alkyl radicals in presence of atomic deuterium is a more rapid process than the deuterization of the saturated hydrocarbons. From the activation energies obtained, values for the bond energies $\text{CH}_3\text{—H}=108$ kcal. and $\text{CH}_3\text{—CH}_3=97.6$ kcal. have been deduced. The discrepancies between these and other values have been emphasized. The uncertainty of the value of the steric factor in the activation energy calculations has been indicated and its influence on the results derived has been exhibited.

AS a supplement to our earlier* work on the interaction of deuterium and methane in the presence of mercury vapor and illuminated by the resonance radiation of mercury, $\lambda=2537\text{\AA}$, we have studied the interaction of atomic deuterium, produced in a modified Wood's hydrogen discharge tube,³ and the aliphatic hydrocarbons methane, ethane, propane and butane. The technique in general follows that described by Bonhoeffer and Boehm⁴ and applied more particularly to hydrocarbons by Bonhoeffer and Harteck,⁵ and by von Wartenberg and Schultze.^{5a} These workers used water vapor in the hydrogen to poison the vessel walls against recombination

of atomic hydrogen, but as Chadwell and Titani⁶ found that hydrocarbons were oxidized to carbon dioxide to 50–80 percent under "wet" conditions, we aimed to employ, as far as possible, dry gases. Smallwood⁷ found that concentrated sulphuric acid acts as a good poison for the hydrogen atom wall recombination and we have followed this procedure.

In addition to the work of Bonhoeffer and Harteck, experiments by Geib and Harteck⁸ have indicated that methane and atomic hydrogen do not interact at temperatures up to 170°C. More recent extension of this work by Geib and Steacie⁹ and by Steacie and Phillips¹⁰ to the interaction of deuterium atoms with methane and ethane confirmed this view and have led to an activation energy for the reaction $\text{CH}_4 + \text{D} = \text{CH}_3\text{D} + \text{H}$ of 11 kcal. Very little exchange was

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* This issue, following paper.

³ R. W. Wood, *Phil. Mag.* **42**, 729 (1921); **44**, 538 (1922).

⁴ Bonhoeffer and Boehm, *Zeits. f. physik. Chemie* **119**, 385 (1926).

⁵ Bonhoeffer and Harteck, *Zeits. f. physik. Chemie* **139A**, 64 (1938).

^{5a} von Wartenberg and Schultze, *Zeits. f. physik. Chemie* **2B**, 1 (1929).

⁶ Chadwell and Titani, *J. Am. Chem. Soc.* **55**, 1363 (1933).

⁷ Smallwood, *J. Am. Chem. Soc.* **56**, 1542 (1934).

⁸ Geib and Harteck, *Zeits. f. physik. Chemie* **170A**, 3 (1934).

⁹ Geib and Steacie, *Zeits. f. physik. Chemie* **B29**, 215 (1935).

¹⁰ Steacie and Phillips, *J. Chem. Phys.* **4**, 461 (1936).

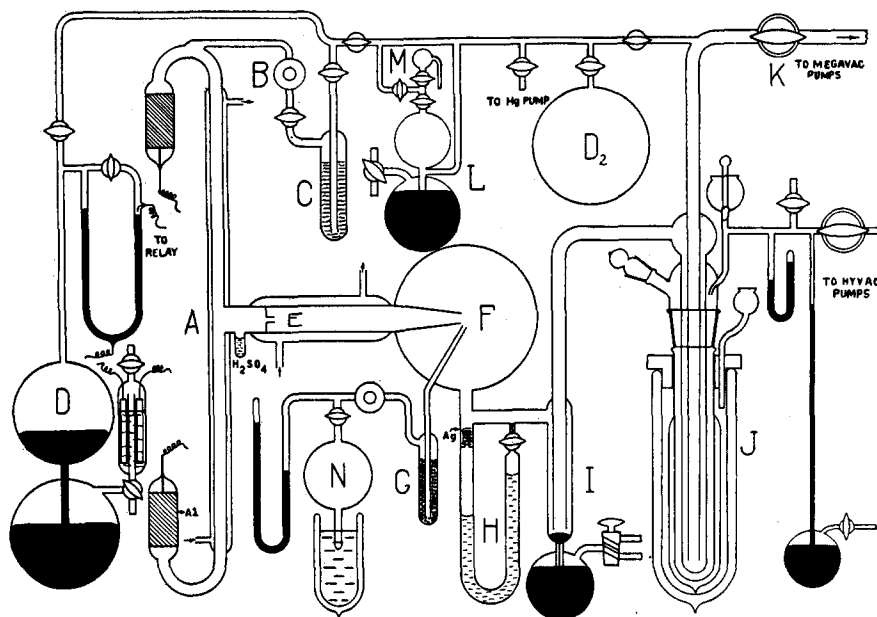


FIG. 1.

secured in the latter work but, with ethane, the production of deuterioethanes by exchange with atomic deuterium at 25°C was claimed. Our own work has been extended to temperatures where appreciable exchange occurs with methane and we have made a more extensive examination of the interactions with the higher hydrocarbons than hitherto, with new and important results.

EXPERIMENTAL DETAILS

Materials used

The preparation and purification of the methane, ethane, propane, deuterium and hydrogen used in this work have already been described in previous reports from this laboratory.¹¹ The butane used was prepared by repeated fractionation of tank butane. As used it may have contained a little isobutane and butylene.

Apparatus and experimental method

The apparatus is shown in outline in Fig. 1. Deuterium or hydrogen was introduced to the discharge tube *A* through an adjustable valve *B*, through a liquid-air trap *C* from a reservoir *D* automatically kept at constant pressure. The discharge tube was water-cooled and poisoned by

allowing to stand under vacuum in an atmosphere of H_2SO_4 vapor when not in use. This sufficed to insure adequate atom concentrations even under dry conditions. The atom stream passed through a 3 mm orifice *E* to the water-cooled connecting tube between discharge tube and reaction vessel *F*.

The hydrocarbon was introduced into the reaction vessel from flask *N* through a solid CO_2 trap *G* packed with copper granules. The two gas streams met and intermixed at two jets located centrally in the spherical reaction vessel, 500 cc in volume. The gas pressures were measured on an oil manometer *H* (Apiezon vacuum oil; density = 0.86 at 26°C). The exit gases passed through a mercury cut-off *I* and thence to a special low temperature trap *J* in which the gaseous hydrocarbons were frozen. Test showed that 60–90 percent of the methane was recoverable, thus depending on the prevailing partial pressure. The residual hydrogen isotopes passed on to the pumping system, two megovac pumps in parallel.

The low temperature in trap *J* was attained by evaporating liquid air located around the trap and in two co-axial Dewar vessels, the outer one containing liquid air at atmospheric pressure. The pressure over the liquid air in the inner

¹¹ Morikawa, Benedict and Taylor, *J. Am. Chem. Soc.* **58**, 1445 (1936) and a forthcoming paper by Morikawa, Trenner and Taylor in *J. Am. Chem. Soc.*

vessel was 4 mm corresponding to a temperature of $\sim -230^\circ\text{C}$.

Rates of gas flow were calibrated by measures of the volumes actually consumed from the respective reservoirs during a run. The discharge tube was operated from a 6000 volt 2 kva transformer, the tube current being read directly from an a.c. milliammeter in the tube circuit. A variable resistance in the primary circuit served as a current control.

The D (or H) atom concentration was determined by measuring the extent of exchange in the reaction $\text{H} + \text{D}_2$, the exit gases being analyzed by means of a Farkas thermal conductivity gauge.¹² We employed in our calculations of the atom concentrations from the reaction $\text{H} + \text{D}_2 = \text{HD} + \text{D}$, the data of A. and L. Farkas,¹³ $E = 6.55$ kcal., $k_{299} = 4.9 \times 10^5$ liter mole sec.; steric factor, $s = 0.1$. A blank run, *W1*, with D_2 alone showed a negligible amount of light hydrogen so that reaction with manometer oil, or other light hydrogen sources, is unimportant. The absence of hydrocarbon in the discharge tube was shown by spectroscopic observation of the light emitted in the discharge and by calculation of the back diffusion against a linear velocity of flow reaching 2400 cm per sec. through the orifice *E*.

The temperature of the reaction vessel when hot was attained by surrounding the vessel with an electric furnace. All temperatures cited are mean temperatures from several thermometers located at different places within the furnace. The temperature control was manual.

Operating conditions

Normal operating conditions were: Total pressure, 0.5 mm Hg; deuterium flow rate, 600 cc per hour at N.T.P.; hydrocarbon flow rate, 100 cc per hour S.T.P.; contact time, 1.8 sec.; arc current, 350 ma; D atom concentration, 10 to 20 percent; temperature of trap *J*, $\sim -230^\circ\text{C}$; duration of run, ~ 1 hour. The discharge tube was always operated for 0.5 hour before the hydrocarbon was introduced; the D_2 hydrocarbon ratio was adjusted by pressure.

After about 100 cc hydrocarbon were passed, the cut-off *I* was raised and the low temperature trap *J* was thoroughly evacuated for 10–15

minutes and the trap finally isolated by closing the main stopcock *K* to the pumps. The liquid air in the inner Dewar vessel was then raised to normal temperature by raising the pressure over it to atmospheric pressure. The methane present in the trap now showed a measurable vapor pressure and was removed by a Töpler pump *L* to a sampling tube *M*. After methane removal, the trap was raised in temperature to -78°C and the next higher fraction was collected in a sampling tube *M* by means of the Töpler pump. Finally, the trap temperature was raised to room temperatures and any residual vapors pumped off with the Töpler pump and put into a sampling tube for future analysis. These latter samples throughout the investigation contained only traces, i.e., less than 0.5 percent, of higher hydrocarbons and water. No carbon dioxide was found.

The details of the fractionation purification procedure for these samples will be described elsewhere,¹⁴ as it has general applicability. The methane fraction was passed over copper oxide at 270°C to remove traces of hydrogen isotopes. This does not cause any exchange.¹¹ It was fractionated once more from liquid air to remove traces of higher hydrocarbons. The total volume thus received was measured and then analyzed for exchange by means of a thermal conductivity gauge developed by one of us (N.R.T.).¹⁵

The fractions containing higher hydrocarbons received the following treatment. Residual methane was removed by a Töpler pump at liquid-air temperatures and the amount thus recovered was measured. The residue was hydrogenated with light hydrogen on catalytic copper at 60°C to remove possible traces of olefines.

These latter never exceeded 1 percent even when estimated before or after separation of methane. The excess hydrogen was removed on copper oxide at 300°C and by evacuation at liquid-air temperature. In the ethane runs the residual ethane was fractionated into several samples, the first and last samples were rejected and the middle samples collected for exchange analysis. In the propane experiments this final fractionation was conducted to give an ethane-rich fraction containing small amounts of propane

¹² We are indebted to Mr. E. A. Smith of this laboratory for these analyses.

¹³ A. and L. Farkas, Proc. Roy. Soc. **152**, 147 (1935).

¹⁴ Morikawa and Trenner, J. Am. Chem. Soc. forthcoming paper.

¹⁵ N. R. Trenner, J. Chem. Phys. forthcoming paper.

and a propane-rich fraction from which a middle cut gave a sample for exchange analyses.

In order to avoid possible errors in the thermal exchange analyses of the hydrocarbons due to the presence of other hydrocarbons as a result of improper fractionation the several middle cuts were always thermally analyzed and, unless all cuts agreed, the results were rejected and the whole subjected to refractionation and thermal analysis until such agreement was obtained, when pure gas fractions were obviously being studied. Very few such refractionations were required, proving the precision of our separation methods. Further, the composition of the ethane sample was ascertained by reaction with hydrogen on a nickel catalyst at 300°C to yield methane whence the value of n in C_nH_{2n+2} could be determined. In the case of butane, the higher hydrocarbons were separated into ethane, propane and butane cuts by repeated refractionations and samples of middle cuts reserved for exchange analysis.

A special analysis of the ethanes from runs W15, 16 and 19 was made. The ethane fractions

from each were combined and carefully refractionated. The C_2 fraction (17.4 cc) was divided into two portions. On one, a hydrogenating decomposition to methane on nickel gave a formula $C_2H_{5.6}$ for the fraction. The second portion was hydrogenated on copper with H_2 to convert olefines to saturated hydrocarbons. 8 percent of the whole fraction was thus found to be C_2H_4 . The excess hydrogen was then removed by evacuation at liquid-air temperatures with the Töpler pump and reserved for exchange analysis. The deuterioethane was freed from traces of hydrogen by copper oxide and also reserved for exchange analysis. Less than 1 percent deuterium was found in the hydrogen thus also confirming the absence of large amounts of olefines since these exchange with hydrogen over copper at 65°C.¹⁶ As shown in Table I, the ethanes analyzed 50.8 percent C-D bonds. We shall deal later with the significance of this result.

¹⁶ Morikawa, Trenner and Taylor, J. Am. Chem. Soc. forthcoming paper.

TABLE I. Results of D + hydrocarbon reactions.

RUN No.	HYDROCARBON USED	TEMP.	PRESS. RATIO	HYDROCARBONS RECOVERED					HYDROCARBON	EXCHANGE		
				Methane		Ethane cc	Propane cc	Butane cc		Decomposed in Percent	in % = $\frac{C-D}{C-H+C-D} \times 100$ $\frac{CH_4}{C_2H_6 \quad C_3H_8}$	
	cc (1 atmos. & 25°C)	°C	D ₂ : HC mm of oil ^d	cc	% Recov.							
W2	CH ₄ +H 219	28	5 : 0.25 mm H ₂ SO ₄	153	70	0 CO ₂ and	0 higher HC	0 =neg- ligible	Olefines absent to — 1% in all runs	—	—	—
W3	CH ₄ +D 73	28.4	4 : 0.2 mm H ₂ SO ₄	62	85	—	—	—		0 (by infrared)	—	—
W6	CH ₄ +D 90	26.3	5 : 0.45	85	94	—	—	—		0	—	—
W9	CH ₄ +D 83.4	103	6.3 : 0.4	76.5	92	—	—	—		0	—	—
W11	CH ₄ +D 93.8	165	6.1 : 0.8	70	74.6	—	—	—		0	—	—
W12	CH ₄ +D 81.0	208	6.0 : 0.4	70	86.4	—	—	—		0	—	—
W17 ^c	CH ₄ +D 79.5	310	6.0 : 0.5	63.7	80.2	—	—	—		9.6	—	—
W7	C ₂ H ₆ +D 131 (calc.)	27.3	4.5 : 0.75	16.9	60 (assumed)	117	—	—	10.6	53.5	0	—
W8	C ₂ H ₆ +D 94 (calc.)	103	6.8 : 0.40	27.0	60 (assumed)	71.2	—	—	24.2	46.5	0	—
W10	C ₂ H ₆ +D 98	166	5.7 : 0.8	21.0	55.0	78.9	—	—	19.5	35.0	7.0	—
W13	C ₂ H ₆ +D 97.3	208	6.0 : 0.5	16.0	52.3	82.0	—	—	15.7	53.0	13.6	—
W14 ^c	C ₂ H ₆ +D 86.4	25	6.0 : 0.5	24.7	81.2	68.5	—	—	20.7	63.0	0	—
W18 ^c	C ₂ H ₆ +D 90.8	110	6.0 : 0.5	26.8	68.0	71.1	—	—	21.6	50.7	3.6	—
W20 ^c	C ₂ H ₆ +D 92.2	192	6.0 : 0.5	12.4	49.2	79.5	—	—	13.8	47.5	9.1	—
W15 ^c	C ₃ H ₈ +D 99.5	24.7	6.0 : 0.5	4.3	71.7	≥ 0.8	97.0	12.5	2.4	90.5	50.8	0
W16 ^c	C ₃ H ₈ +D 89.3	109	6.0 : 0.5	11.1	69.6	≥ 6.3	79.8		10.6	60.0		0
W19 ^c	C ₄ H ₁₀ +D 93.3	110	6.0 : 0.5	10.1	—	4.9	3.2	83.0	11.0	72.5		0
W1 ^a	D alone	26.5	3.5 mm H ₂ SO ₄	—	—	—	—	—	—	—	—	—
W5 ^b	D ₂ +H	26.5	$\begin{cases} H_2 : D_2 \\ 4.9 : 2.6 = 7.5 \end{cases}$	—	—	—	—	—	—	—	—	—

^a Percent D₂ used = 98.5 percent; percent D₂ recovered 97.5 percent; ∴ exchange negligible.

^b In W5 the H atom concentrated calculated to be 9.4 percent giving 34 mole percent of HD in a contact time of 1.8 sec. in a system of 39 atom percent D and 61 atom percent H at a total pressure of 0.49 mm Hg. Temperature = 26°C.

^c Experiments marked c were run with an initial D atom concentrate of about 20 percent, the others with about 9–10 percent D atom concentrate.

^d Values of pressure are given in mm of oil except where otherwise indicated.

The efficiency of the fractionation procedure can be ascertained from this last example. The amount of ethane recovered from *W19* is more accurately known because of favorable fractionation conditions, the propane content was small, and amounted to 4.9 cc. The combined C_2 fraction in *W15*, 16 and 19 was 17.4 cc or $17.4 - 4.9 = 12.5$ cc from *W15* and 16. A direct single fractionation in *W15* and 16 separately gave a total of 7.1 cc. The ethane total in *W15* and 16 obtained by the subtraction process is smaller than the methane recovered in these runs, 15.4 cc, which is only 70 percent of the total methane formed in the reaction.

Experimental results

Although our general operating conditions were rather similar in every respect to those employed by Bonhoeffer and Harteck⁵ in their investigations of the reactions induced in the aliphatic hydrocarbons by hydrogen atoms, with the exception that dried gases were employed by us while the former workers used wet hydrogen, we did not observe the luminescence which they reported. We are somewhat at a loss to account for this but suggest that it may be associated with the use of wet hydrogen which Chadwell and Titani⁶ found, as previously indicated, always resulted in considerable oxidation to carbon dioxide of the alkyl halides studied by them. We feel that the fact that the spectrum associated with this luminescence was, to quote from Bonhoeffer and Harteck's paper, "the spectrum of burning hydrocarbons" is significant when considered in the light of Chadwell and Titani's results and may be associated with the oxidation processes of the type studied by Geib and Harteck.⁸ We did not find appreciable amounts of unsaturated products as reported by these former workers although carefully sought. We shall discuss reasons for this later.

In comparing our results on all hydrocarbons *above methane* with those of Bonhoeffer and Harteck it should be borne in mind that the temperature in their reaction system was quite high, estimated to be 300° at the center of the reaction zone, while in our case measurement within the reaction region showed only a few degrees rise at room temperatures. This, as will be indicated later, somewhat changes the nature

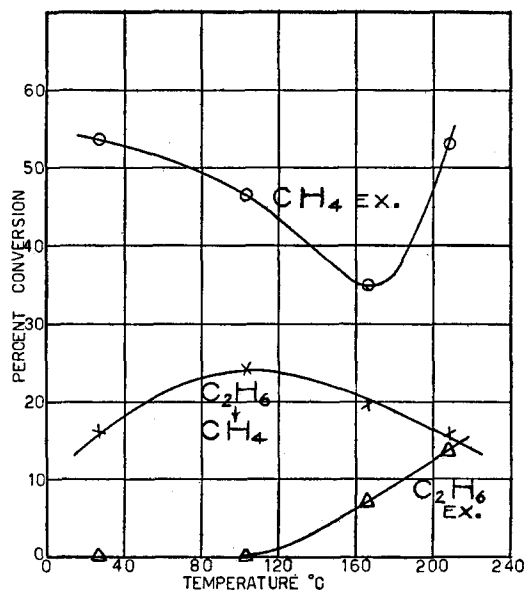


FIG. 2.

of the reactions involved and may account for some of the differences observed. In the case of methane no such temperature rise occurred in Bonhoeffer and Harteck's experiments.

The results are summarized in Table I. Two D atom concentrations were used, 10 and 20 percent, the latter indicated by a letter *c*.

The methane reaction

No exchange occurred between 25 and 208°C. At 310°, a definite exchange of 10 percent occurred. Under the experimental conditions this corresponds to a *minimum* activation energy of 15.6 kcal., when the relative rates of $H + D_2$ and $D + CH_4$ are compared. The minimum value arises from the fact that the mean rate of HD formation over a period of time was measured, not the initial rate which is certainly greater. A calculation based on the absolute rate of reaction at 310°C gives a value of $E = 18$ kcal. which we regard as an *upper* limit. The calculation employs the kinetic expression $v = sZe^{-E/RT}$. For *Z* we write

$$10^{28.44} C_1 C_2 (\sigma_1 + \sigma_2)^2 \left(\frac{T(M_1 + M_2)}{M_1 M_2} \right)^{\frac{1}{2}},$$

where $\sigma_D = 2.1 \times 10^{-8}$, $\sigma_{CH_4} = 3.8 \times 10^{-8}$, $T = 583^\circ K$ and $C = P/T = 62.35 \times 10^{-3}$. The total working pressure was 0.41 mm Hg composed of 6 parts D_2 to 1 part of hydrocarbon or 0.07 mm CH_4 and

0.034 mm D on the basis of a 10 percent D atom concentration. This yields for the concentration terms $C_D = 0.94 \times 10^{-9}$ mole/cc and $C_{CH_3} = 1.93 \times 10^{-9}$ mole/cc. This yields a value for $Z = 3.15 \times 10^{-3}$ mole/cc/sec., whence, with a steric factor $s = 0.1$, we deduce from $v = 3.22 \times 10^{-11}$ mole/cc/sec. a value for $E = 18.7$ kcal. If the D atom concentration were as low as 5 percent, the corresponding E would be 17.9 kcal. Additional uncertainties in this calculation are the steric factor $s = 0.1$ and the assumption that the rate of CH_3 production is one-third the rate of C-D bond formation owing to the rapid exchange occurring with CH_3 radicals as revealed in subsequent data.

Both the upper and lower values for E are, however, definitely greater than the value $E = 11.5$ kcal. reached by Steacie and Phillips from the mercury photosensitized reaction and this is true also for the corresponding data of Morikawa, Benedict and Taylor,¹⁷ indicating that this quantity cannot be determined readily by photosensitization experiments.

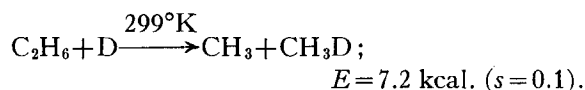
The ethane reaction

Decomposition by atomic deuterium to form methane occurs from 27° upwards but ethane exchange does not measurably occur under our conditions below 100°. This latter result differs sharply from that recorded by Steacie and Phillips. Our observation is strengthened by the similar absence of exchanged propane and butane in Expts. W15, 16 and 19 at temperatures from 25° to 110°C. Above 100°, we find increasing ethane exchange with increasing temperature. Typical results are given in Fig. 2.

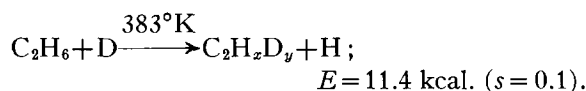
In respect to the methane formed we direct attention especially to the high D content of the product. In one experiment W14, this reaches the high value of 63 percent, which, upon a basis of primary split to yield $CH_3 + CH_3D$, requires that the methyl radical be completely exchanged to CD_3 before stabilization as a deuteromethane molecule CD_4 . In all the other ethane experiments, while not so complete as in W14, extensive D substitution in the methane has occurred. This result is confirmed by the extensive C-D bond content of the composite ethanes from propane and butane.

¹⁷ Morikawa, Benedict and Taylor, J. Chem. Phys. 5, 212 (1937).

Calculations from the absolute rates of reaction analogous to that outlined in the case of methane give the following activation energies. For the C-C bond split in ethane to yield methane at 26°C we calculate



For the exchange reaction at 110°C we obtain



This latter value is greater than that calculated by Steacie and Phillips, $E = 6.3$ kcal., based on reaction at room temperature.

The propane and butane reactions

The striking features of these reactions in addition to the deuterium content of the ethanes produced are the relatively small decomposition of these hydrocarbons and, again, the high degree of deuterio-substitution of the methanes produced. Comment has already been made on the excess of methane formed over ethane from propane and over propane from butane.

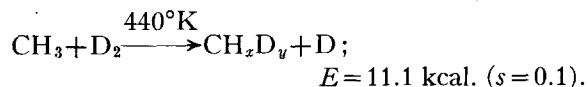
Comparison of the total consumption of D atoms actually used in reaction at low temperatures (110°C) can be estimated from the data presented in runs W16, 18 and 19, Table I. Rounding off decimals as unimportant for our present purposes and bearing in mind that exchanges of type $CH_3 + D \rightarrow CH_2D + H$ do not remove H atoms we find 44 cc of methane formed in W18 which obviously involves the consumption of 44 cc of D atoms. Since in all these cases 60 cc of D atoms were engaged we find 16 cc of these D atoms are unused by the ethane and must recombine on the walls. In the case of propane, W16, the figures are 24 cc of split hydrocarbon products equivalent to 24 cc of D atoms used or 36 cc of D atoms unused. Similarly in the case of butane, W19, a total of 24 cc of split products were formed which corresponds to 36 cc of D atoms unused as in the case of propane. This relatively smaller reactivity of the higher hydrocarbons over that displayed by ethane is, we feel, due to a kind of greater steric hindrance in the former cases to the approach of a D atom possessed by virtue of their "cork screw" con-

figuration. This steric hindrance effect is greater in its reducing effect upon the reactivity than the increasing influence by virtue of the somewhat similar C—C and C—H bond strengths which exist in these higher hydrocarbons. In any case we cannot see the need nor evidence for the introduction of the Bonhoeffer and Harteck postulation of a "catalytic" recombination effect of the higher hydrocarbon molecules by means of a hydrogenation-dehydrogenation mechanism for the explanation of our results. About 50 percent of the introduced D atoms are on the average consumed in splitting reactions, the remainder cleaning up on the walls etc., diffusion to the walls being not excessively slow at our low pressures for fast moving H atoms in the narrow connecting tubing encountered on leaving the reaction vessel. Subsequent more exact measurements of the relative temperature coefficients involved may decide the adequacy of our steric postulate to account for the smaller reactivity of propane and butane over the existence of real activation energy differences which our present data do not seem to show.

DISCUSSION OF RESULTS

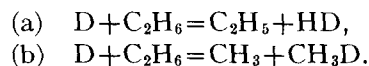
Reaction mechanisms

The evidence available in the interaction of atomic deuterium with methane which only occurs measurably in the neighborhood of 300°C in the present work does not permit a decision between the two alternative processes (a) $\text{CH}_4 + \text{D} = \text{CH}_3\text{D} + \text{H}$ and (b) $\text{CH}_4 + \text{D} = \text{CH}_3 + \text{HD}$ followed by reaction of the methyl radical. However, we know from our earlier work¹⁷ and the present work with ethane that methyl radicals readily react with molecular hydrogen at temperatures above about 165°C. For this reason we deduce an activation energy for the reaction:



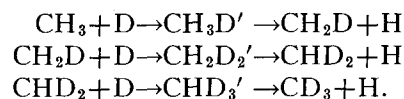
At room temperatures such a reaction does not occur measurably, so that we must consider other methods of methane formation from the methyl radicals produced by atomic deuterium in the C—C bond split of ethane which freely occurs at room temperature. There are two possible alter-

native initial steps in the interaction with ethane:

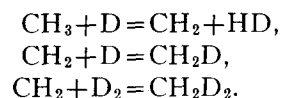


The first corresponds to the primary step in the Bonhoeffer-Harteck suggestion of a dehydrogenation-hydrogenation mechanism of "catalytic" recombination of atomic hydrogen. It would be followed by further dehydrogenation to ethylene on rehydrogenation to deuterioethanes. The negligible amounts of unsaturated products (~1 percent) and the absence of exchanged ethanes in the low temperature runs indicate that this reaction cannot be very important. The extensive methane formation at room temperatures indicates that reaction (b) has a small activation energy of 7.2 kcal., as previously stated.

The extensive deuterium substitution of the resulting methanes suggests that one or both products of the split must undergo further interaction with deuterium atoms (at ordinary temperatures, as seen above, reaction of methyl with hydrogen molecules is of low efficiency). The mechanism for the deuterization of the methyl radicals is easily understood. It may follow a sequence of processes such as:

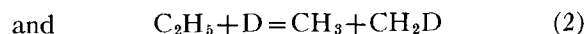
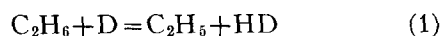


This represents the formation and dissociation, before stabilization by third body collision, of quasi-methane molecules. The experimental condition of high D atom concentration relative to H would insure fairly complete conversion of CH_3 to CD_3 . This would suffice to account for the observed deuterium exchanges. An alternative mechanism to this would involve dehydrogenation-rehydrogenation, thus:



There is no evidence for or against this mechanism.

We cite as additional reason for reaction (b) as opposed to a sequence of reactions:



for the C—C bond split, the earlier experiments with Hill¹⁸ in which the addition of hydrogen atoms to ethylene was studied in the temperature range 16–100°C. The evidence there obtained is decisive that the addition, through C₂H₅, to ethane was quantitative and complete before any measurable amounts of methane were formed. These data together with those of the present work indicate definitely that at ordinary temperatures the collision C₂H₆+H is a much more important method of securing the C—C bond split than the collision C₂H₅+H.

If the C—C bond in C₂H₅ is strengthened by dehydrogenation of C₂H₆ as certainly is the case when still further dehydrogenation to C₂H₄ occurs then one sees at once the reason for the results of Taylor and Hill and those found in the present investigation both of which point to the fact that C₂H₆ under the influence of H atoms splits directly to CH₃ and CH₄ at least at low temperatures.

Above 100°C the deuterization of ethane becomes marked. We ascribe this to the more frequent occurrence of the dehydrogenation reaction C₂H₆+D=C₂H₅+HD followed by the recombination of C₂H₅ and D to yield deuterioethanes, as in the experiments of Taylor and Hill. A repetition of such processes as C₂H₅+D→C₂H₅D'→C₂H₄D+H₁ increases the substitution. An alternative source of deuterioethanes is present in the recombination process of two methyl radicals, the extent of deuterization being dependent on the deuterium content of the radicals. This recombination process, depending on the square of the methyl concentration, becomes increasingly important with the increase in stationary state concentration of methyl radicals with increase in temperature. Both these methods of producing deuterioethanes are secured at the expense of deuteromethane production which, as Table I shows, decreases in extent beyond 100°, having risen in amount up to that temperature.

At temperatures beyond 165°C the reactions CH₃+D₂=CH₃D+D and C₂H₅+D₂=C₂H₅D+D become important alternative methods of producing substitution (cf. W13 and W20).

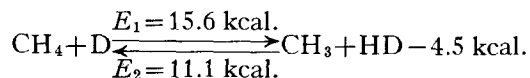
The ready deuterization of methyl radicals as

compared with methane is also observed in the case of the ethyl and propyl radicals from propane and butane. We may adopt a similar explanation, namely the formation and dissociation, before stabilization by third body collision, of "hot" quasi-propane and -butane molecules. As the yield of methane in every case exceeds the amount equivalent to ethane or propane which should simultaneously be formed we must conclude that a certain amount of further decomposition of these quasi-molecules to split products must occur.

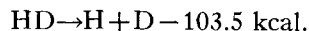
In every case the data reveal that the split products from a hydrocarbon are very highly exchanged. In many cases the extent of exchange borders on the limit of that possible if the process be exemplified by the reaction C₂H₆+D=CH₃+CH₃D and the deuterization of the methyl be complete. The exchange is in several cases so high as to suggest that the formation of CH₃D (and the corresponding ethane and propane with the higher hydrocarbons) does not end the substitution in that fragment of the molecule. Since normal methane molecules do not interact below 300°C this would involve the assumption that the energy available to the molecule CH₃D as a result of its formation (the reaction C₂H₆+D=CH₃+CH₃D is probably 10 kcal. exothermal) is available for further reaction with atomic deuterium. A small amount of such reaction would suffice to account for observed substitutions.

Bond energies

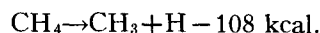
The activation energies which we have deduced for two of the reaction processes in the methane-deuterium system permit an estimate of the magnitude of the CH₃—H bond in methane. We express these activation energies E_1 and E_2 and the consequent heat of reaction ($E_2 - E_1$) by the equation



For each activation energy we have assumed a steric factor $s=0.1$. Combining this with the equation:



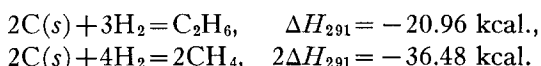
we deduce for the process



¹⁸ Taylor and Hill, J. Am. Chem. Soc. **51**, 2922 (1929).

This is near to the upper limit previously deduced by Polanyi and Hartel¹⁹ (98–110 kcal.) from the reaction in $\text{CH}_4 + \text{H}_2$ systems induced by chlorine and sodium atoms. The value of 108 kcal. is larger than can be derived from an assignment of equal energies to the four C–H bonds in methane. Our calculations show that the value is not very sensitive to the assumptions made as to steric factor, but we hope later, by greater refinements of technique and the study of other reaction systems, to give to the value a definite precision. In the meantime we believe that it cannot be in error by more than 3000 calories.

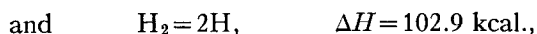
Such a value for the energy of this $\text{CH}_3\text{—H}$ bond when combined with the most recent data on the heats of formation of methane and ethane from solid carbon (diamond) and hydrogen, leads to a startling result for the C–C bond energy in ethane. According to Bischofsky and Rossini²⁰ the heats of formation are



Whence



Since



we derive



This is a surprisingly high result. Earlier values approximate to 80 ± 6 kcal. and values as low as 65 kcal. have been discussed. All these estimates hinge in some way or other on the heat of vaporization of carbon, a factor which has consistently loaded the result with much uncertainty.²¹ It is of interest to note that to bring the value for the C–C bond in ethane down to the value 80 kcal. the value for the $\text{CH}_3\text{—H}$ bond must be lowered to 99.2 kcal. Such a figure would change the order of difference between E_1 and E_2 .

¹⁹ von Hartel and Polanyi, *Zeits. f. physik. Chemie* **11**, 97 (1931).

²⁰ Bischofsky and Rossini, *The Thermochemistry of Chemical Substances* (1936).

²¹ See for example, Goldfinger and Jeunehomme, *Trans. Faraday Soc.* **32**, 1591 (1936).

E_2 would be greater by 4.3 kcal. in which case it would be impossible to account for the relative ease of the reaction $\text{CH}_3 + \text{HD}$ as contrasted with the reaction $\text{CH}_4 + \text{D}$. To bring the energy of the C–C bond down to the value of 72 kcal. recently deduced by Kistiakowsky²² it would be necessary for the activation energy of the reaction $\text{D} + \text{CH}_4 = \text{CH}_3 + \text{HD}$ to be as low as 3 kcal. with a value for the activation energy of $\text{CH}_3 + \text{D}_2 = \text{CH}_3\text{D}$ of 11 kcal. This would be in total disagreement with our observation of the difficulty of interaction between methane and atomic deuterium. We are making further studies of these processes by other methods. The data thus obtained may permit the elimination of the steric factor from the calculation, a factor which must now be used with a considerable degree of arbitrariness.

From an investigation of the concentrations of CH_3 radicals and H atoms present in the photodecomposition of acetaldehyde between 400 and 700°K Patat²³ arrived at the activation energy for the reaction $\text{CH}_3 + \text{H}_2 = \text{CH}_4 + \text{H}$. He found it to be 9 kcal. when the steric factor s was taken to be 10^{-4} . This was done to obtain agreement with von Hartel and Polanyi's directly observed value of 8 kcal. If, however, s be taken as unity then Patat's value becomes 20 kcal. Paneth, Hofeditz and Wunsch's²⁴ data on the direct reaction of CH_3 with H_2 gives an E_{act} of 15 kcal. when $s=1$ Using Geib and Harteck's estimated value of $E_{\text{act}}=17$ kcal. when $s=1$ for the reaction $\text{CH}_4 + \text{H} \rightarrow \text{CH}_3 + \text{H}_2$ but changing s to 10^{-4} Patat finds $E_{\text{act}}=8.7$ kcal. so that:



results. He points out that this result is in essential agreement with Polanyi's previous estimate of 110 kcal. for the C–H bond in methane, deduced from the fact that Cl atoms react rapidly with methane. The present authors intend to investigate the correctness of such a value as 10^{-4} for the steric factor s by a direct estimation of the temperature coefficient of the reaction $\text{CH}_4 + \text{D} \rightarrow \text{CH}_3 + \text{HD}$. We shall report such studies at a later date.

²² G. B. Kistiakowsky, *J. Phys. Chem.* **41** (1937). Symposium on Molecular Structure, Princeton, Dec. 1936.

²³ F. Patat, *Zeits. f. physik. Chemie* **32B**, 290 (1936).

²⁴ Paneth, Hofeditz and Wunsch, *J. Chem. Soc.* 372 (1935).