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Citation: [The Journal of Chemical Physics](#) **4**, 461 (1936); doi: 10.1063/1.1749885

View online: <http://dx.doi.org/10.1063/1.1749885>

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THE JOURNAL OF CHEMICAL PHYSICS

VOLUME 4

AUGUST, 1936

NUMBER 8

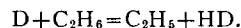
The Reactions of Deuterium Atoms with Methane and Ethane

E. W. R. STEACIE AND N. W. F. PHILLIPS, *Physical Chemistry Laboratory, McGill University, Montreal*

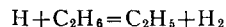
(Received June 13, 1936)

The reactions of deuterium atoms with methane and ethane have been investigated, the atoms being produced by the discharge tube method and by photosensitization with mercury. The activation energies found were 11.7 Kcal. for methane, and 6.3 Kcal. for ethane.

The mechanism of the latter reaction is discussed, and it is concluded that the measured activation energy is that of the reaction



Hence the reaction



must have approximately the same energy of activation. On this assumption the free radical chain theory of first order reactions is discussed in the light of the recent work of Patat and Sachsse.

INTRODUCTION

SINCE the discovery of the heavy hydrogen isotope, the kinetics of a considerable number of exchange reactions have been investigated. Reactions involving atoms are among the most interesting of this type, and an investigation of the reactions of deuterium atoms with water, ammonia, acetylene, and methane has already been described.¹ In this investigation high concentrations of deuterium atoms, produced by the Wood-Bonhoeffer method,² were used and the following activation energies were found:

$\text{D} + \text{H}_2\text{O}$	11 Kcal.
$\text{D} + \text{NH}_3$	11 Kcal.
$\text{D} + \text{C}_2\text{H}_2$	< 5 Kcal.
$\text{D} + \text{CH}_4$	> 11 Kcal.

Prior to the publication of the above results, a note appeared by Taylor, Morikawa, and Benedict³ describing an investigation of the

¹ Geib and Steacie, *Zeits. f. physik. Chemie* **B29**, 215 (1935); *Trans. Roy. Soc. Can.* **3**, 91 (1935).

² Bonhoeffer, *Zeits. f. physik. Chemie* **113**, 199 (1924); **116**, 391 (1925).

³ Taylor, Morikawa and Benedict, *J. Am. Chem. Soc.* **57**, 383 (1935).

reaction between deuterium atoms and methane. In their experiments the atomic deuterium was produced by photosensitization with mercury. They state that the activation energy of the reaction is of the order of 5 Kcal., which is in sharp contrast to our value of >11 Kcal.

In view of the discrepancy it was considered desirable to reinvestigate the reactions of deuterium atoms with saturated hydrocarbons. We have therefore investigated the reaction with ethane by the Wood-Bonhoeffer method, and the reactions with methane and with ethane by photosensitization with mercury.

A. EXPERIMENTS WITH DEUTERIUM ATOMS PRODUCED BY A DISCHARGE

The apparatus employed was of the usual type, hydrogen being run at very high rates of flow through a discharge tube, the atomic hydrogen thus produced being mixed with the other reactant, and the products removed from the flowing stream and later analysed. The apparatus was, in the main, similar to that previously employed.¹

The discharge was operated on alternating current at about 3000 volts, the current through the tube being maintained constant at 325 milliamperes. Deuterium was stored in a gas-holder at atmospheric pressure, and entered the system through calibrated capillary flow-meters. It passed through the discharge at a streaming velocity of about 1 liter per second, and a pressure of about 0.3 mm, and entered a reaction vessel of about 1 liter capacity. In this vessel it was mixed with the other reactant, and after a contact time of about 1 second the mixture passed out of the reaction vessel and over some gold foil which destroyed the remaining deuterium atoms. The walls of the discharge tube and the reaction vessel were coated with phosphoric acid in the usual way to cut down the rate of recombination of the atoms. The pumping system consisted of a three stage diffusion pump backed by an oil pump. The speed at the entrance to the pump was about 20 liters per second.

Runs were comparatively short in order to conserve deuterium. For this reason the atom concentration in the reaction vessel was determined indirectly by calibrating the apparatus with ordinary hydrogen, and the atom concentration of the deuterium in an experiment was inferred from the current flowing through the discharge. The calibration was made with a Wrede diffusion gauge.⁴ The average atom concentration in a number of calibration runs was 20 percent.

After the gases had passed through the reaction vessel it was necessary to separate the methane or ethane from the deuterium. The vapor pressures at liquid air temperature were too high to permit a simple freezing out. Also, it was impossible to introduce an adsorbent into the main vacuum line, since the resistance thus introduced would cut down the pumping speed enormously. The reactants were therefore separated by adsorption on silica or alumina gel at -180° in a trap between the diffusion pump and the oil pump. Blank runs showed that methane and ethane could be very efficiently separated from hydrogen in this way. After separation the gas was desorbed by warming the gel to

-80° , and was allowed to expand into a combustion vessel where it was burned in dry air on a platinum filament. Since the desorption was carried out at -80° , there was no danger of contamination from traces of residual water which might have been present in the gel. The deuterium content of the resulting water was then determined by measuring the heat conductivity of the saturated vapor as previously described.¹

Deuterium was prepared by the electrolysis of alkaline heavy water. It was passed through a tube filled with platinized asbestos at 500° to remove oxygen, dried by passage through a liquid air trap, and stored in a gas-holder over mercury. Methane and ethane were procured in cylinders from the Ohio Chemical Co. Ethane was purified by repeated fractional distillation. Methane was passed through ammoniacal cuprous chloride, dilute and concentrated sulphuric acid, a 50 cm column of copper oxide at 300° , concentrated potassium hydroxide solution, and Fieser's solution. It was then dried by passage through a trap at -80° , and repeatedly distilled. Acetylene was prepared from calcium carbide and water, washed with sodium hydroxide, and fractionally distilled.

Results with ethane

The results for ethane are given in Table I. The calculations were made as described in the previous papers. In column 5 is given the average time during which a molecule of the reactant is in the reaction space. This is calculated from a knowledge of the amount of gas flowing, the pressure in the reaction vessel, and the volume (920 cc) and temperature (20°) of the reaction vessel. A correction is applied for the increase in volume due to the fact that some of the hydrogen is present as atoms. $Z_{C_2H_6, D}$ in column 7 represents the average number of collisions of 1 ethane molecule with deuterium atoms during the time it is in the reaction vessel. It is calculated assuming a molecular diameter of 3.75×10^{-8} cm for ethane, and of 2.14×10^{-8} cm for a deuterium atom (assumed equal to the collision diameter of a hydrogen atom as found by Harteck).⁵ The values of the "percent

⁴ Wrede, *Zeits. f. Instrumentenk* **48**, 201 (1928); Harteck, *Zeits. f. physik. Chemie* **A139**, 98 (1928).

⁵ Harteck, *Zeits. f. physik. Chemie* **A139**, 98 (1928).

TABLE I. *The reaction of deuterium atoms with ethane.*

DEUTERIUM FLOW=0.202 cc/sec. at N.T.P.					AVERAGE ATOM CONTENT = 20%					
Run No.	Remarks	Pressure (mm)	C ₂ H ₆ , cc/sec. at N.T.P.	Reaction Time (sec.)	P _D (cm)	Z _{C₂H₆, D} (×10 ⁻⁵)	% D Content of ethane	% Exchange	Collision Yield (×10 ⁶)	E (cal.)
1	Blank, no discharge	0.27	0.049	1.11	—	—	0.0	0.0	—	—
2	0.28	0.049	1.15	0.0046	7.8	10.7	18.5	1.5	6400
3	Blank, ethane alone, D ₂ through discharge later	—	0.047	—	—	—	0.0	0.0	—	—
4	0.28	0.044	1.17	0.0047	8.3	14.4	23.7	1.7	6350
5	0.28	0.044	1.17	0.0047	8.3	16.4	27.0	2.0	6250
6	0.28	0.037	1.20	0.0048	8.5	19.8	30.6	2.2	6200
7	0.28	0.034	1.22	0.0048	8.5	17.9	27.0	1.9	6300
8	Blank, D ₂ through discharge alone, ethane later	—	0.033	—	—	—	1.0	1.5	—	—
										mean = 6300

exchange" in column 9 are calculated on the assumption that at equilibrium the distribution coefficient

$$\frac{\text{D/H in ethane}}{\text{D/H in hydrogen}} = 1.$$

In calculating the collision yields in column 10 allowance has been made for the fact that 6 fruitful collisions are required to convert a molecule of C₂H₆ to C₂D₆. The activation energies in the last column are calculated assuming a steric factor of 0.1.

The results lead to an activation energy for the exchange reaction of about 6300 calories. This is much lower than the value for methane, >11 Kcal., previously obtained. This is not surprising in view of the fact that methane has been previously reported to be without appreciable effect on hydrogen atoms, while ethane "catalytically" destroys them to a considerable extent.⁶

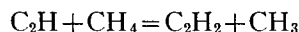
Results with methane-acetylene mixtures

It was shown in the previous paper by Geib and one of us¹ that the reaction D+C₂H₂ had a very low activation energy, *viz.* <4500 calories. On the basis of the discussion in a later section, it seems almost certain that the main primary reaction is



⁶ v. Wartenberg and Schultze, *Zeits. f. physik. Chemie* B2, 1 (1929).

The reaction between deuterium atoms and methane, however, has a high activation energy and consequently shows no exchange with deuterium atoms under our experimental conditions. It therefore appeared possible that some information might be obtained by bringing together deuterium atoms and a mixture of methane and acetylene, and determining whether the reaction



occurred. If it did we would then have



and the methane should be partially exchanged.

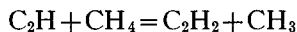
The experimental procedure was identical with that previously described, except that the gases leaving the reaction vessel were first passed through two liquid air traps to freeze out the acetylene. The methane was then frozen out with silica gel as before, burned, and the water analyzed. The acetylene was burned and analyzed in a few cases. It may, however, have been contaminated with some dissolved methane. Since the methane was taken out last, however, there was no danger of it being contaminated with acetylene.

The results are given in Table II. It is evident that a small apparent exchange takes place. This, however, is of the same order of magnitude as in the run with methane alone, and in the previous investigation. It is also independent of

TABLE II. *Methane-acetylene mixtures.*

Run No.	Remarks	Pressure (mm)	CH ₄ cc/sec. at N.T.P.	C ₂ H ₂ cc/sec. at N.T.P.	% D Content of Methane	% D Content of Acetylene
9	Methane only	0.31	0.053	0.0	1.9	—
10	Acetylene only	0.29	0.0	0.049	—	38.7
11		0.30	0.040	0.013	2.9	38.7
12		0.28	0.028	0.010	2.9	31.4
13		0.27	0.013	0.017	2.5	—
14		0.27	0.0062	0.018	2.2	—
15	Blank, no discharge	0.27	0.0052	0.015	0.5	—

the C₂H₂/CH₄ ratio, which was varied over fairly wide limits. It therefore seems certain that the effect is due merely to a small amount of impurity in the methane. Hence, within the experimental error, the reaction



does not occur. The reaction therefore has an activation energy greater than about 8000 cal., in agreement with previous assumptions about reactions of this type.

B. DEUTERIUM ATOMS PRODUCED BY PHOTOSENSITIZATION

The apparatus employed was of the usual static type. The reaction vessel, a cylindrical fused quartz bulb of about 140 cc capacity, was arranged so that measured amounts of various gases could be introduced and the pressure could be continuously observed. It contained a small pool of mercury. The vessel was immersed in a thermostat filled with distilled water at 23°C.

The light source was a Hanovia Resonance Lamp, consuming 100 milliamperes at about 5000 volts. With this lamp almost all the emitted light is in the resonance line at 2537Å. The light passed through a quartz tube, cemented into the side of the thermostat, filled with acetic acid solution. The tube thus acted as a window, a condensing lens, and a filter. This arrangement was not very efficient, and reflection losses from the cylindrical vessel were high. As a result the intensity was low considering the source used, and rather long exposures were necessary.

The intensity of the absorbed light was inferred from measurements of the rate of the mercury photosensitized combination of hydro-

gen and oxygen under identical conditions. It was assumed that 5 molecules of (hydrogen + oxygen) disappeared per quantum of light absorbed.⁷ An average value of 8.77×10^{12} quanta per cc per sec. was found.

In general deuterium was in considerable excess, the experimental mixture being usually about 4D₂+1CH₄. The total pressure was in the neighborhood of 60 cm. After illumination the reactant was separated from the hydrogen, burned, and the deuterium content of the water determined as before.

As mentioned in the previous section, efficient separations of methane or ethane from hydrogen could be made by adsorption on silica gel at -180°. These had been accomplished in a flow system at moderately low pressures. At first it was not realized how sensitive the method was to experimental conditions, and the products were separated as follows:

(A) The methane-hydrogen mixture was kept in contact with alumina gel at -180° for 10 minutes. The system was then evacuated with an oil pump for 10 minutes, and the gel was warmed to -80° to desorb the methane.

(B) As in (A) but using silica gel.

These procedures gave rather high blank values, i.e., accomplished only a partial separation, as is shown by Table III, so the technique was modified as follows:

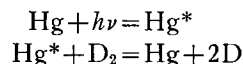
(C) The gases were pumped through silica gel at -180°, and the pumping was continued for 10 minutes. The methane was desorbed at -80° as before.

(D) As in (C) but using higher pumping speeds.

The separations thus effected were quite satisfactory, the blanks being reduced to about 2 percent.

The results for methane are given in Table III.

In order to calculate the collision yield, and hence the activation energy, it is first necessary to evaluate the stationary concentration of deuterium atoms produced by the illumination. The initial reactions



have been directly evaluated, since we have used the hydrogen-oxygen reaction as an actinometer. We may assume that the quenching effect of methane is negligible.⁸ The wall deactivation of excited mercury atoms is also

⁷ See, for example, Jungers and Taylor, J. Chem. Phys. **3**, 338 (1935).

⁸ Zemansky, Phys. Rev. **36**, 919 (1930).

negligible for the gas pressures employed. The initial process will be followed by

- (1) $D + D + M = D_2 + M$
- (2) $D = \frac{1}{2}D_2$ (wall)
- (3) $D + CH_4 = CH_3D + H$ (or other products which use up D atoms).

We may neglect the reaction $H + D + M = HD + M$, since for small percentage conversions there will be an inappreciable quantity of atomic hydrogen present. Hence we may write

$$\frac{d}{dt}[D] = \frac{2I_{\text{abs.}}}{N} - K_1[D]^2[M] - K_2\frac{[D]}{[M]} - K_3[D][CH_4] = 0,$$

where N is Avogadro's number, and M is a third body.

The rate of recombination of hydrogen atoms under directly comparable experimental conditions has been investigated by Farkas and Sachsse,⁹ who found that at pressures higher than 20 cm the term $K_2[H]/[M]$ could be neglected, and estimated K_1 (for H atoms) to be $3.4 \times 10^{16} \text{ cm}^6 \text{ mole}^{-2} \text{ sec}^{-1}$. There is a marked discrepancy between this result and those obtained by discharge tube methods.¹⁰ In Farkas and Sachsse's experiments the rate constant given is based on the assumption that "M" is H_2 . Smallwood found 1.7×10^{16} for the case where

⁹ Farkas and Sachsse, *Zeits. f. physik. Chemie* **B27**, 111 (1935).

¹⁰ Amdur and Robinson, *J. Am. Chem. Soc.* **55**, 1395 (1933); Smallwood, *ibid.*, **56**, 1542 (1934).

M is a hydrogen atom, and stated that the constant for the reaction $H + H + H_2$ was at least 50 times smaller. The two values for the latter reaction differ, therefore, by a factor of 100. The conditions in the two investigations were, however, widely different, since Farkas and Sachsse worked at pressures of the order of atmospheric and used minute H atom concentrations, while the other investigations were made with high H atom concentrations and pressures of the order of a millimeter.

Since the conditions in our experiments were almost identical with those of Farkas and Sachsse, we will adopt their value for the rate constant of the reaction $H + H + H_2$. It should be noted that Farkas and Sachsse *measured* the stationary hydrogen atom concentration and calculated the rate constant from it. Since we are using their values of the rate constant to calculate the stationary hydrogen atom concentration under almost identical conditions, we are in effect merely using their measured values of the hydrogen atom concentration. The values calculated in this way should therefore be but slightly influenced by any errors in Farkas and Sachsse's mechanism and calculations, and dependent only on the accuracy of their measurements of the stationary hydrogen atom concentration.

The above discussion refers, of course, to hydrogen, not deuterium. It may be assumed that the only difference between the two will be in the frequency of triple collisions. Tolman¹¹

¹¹ Tolman, *Statistical Mechanics* (Chemical Catalog Co., New York), p. 245.

TABLE III. *The photosensitized reaction between deuterium and methane. Temperature 23°C.*

Run No.	Time of Illumination (sec.)	P_{D_2} (cm)	P_{CH_4} (cm)	Method of Analysis	D Content of Methane (%)	D Atom Concentration (moles/cc)	Fraction of Methane Converted per sec.	E (Kcal.)
1	0.95×10^5	39.6	9.5	A	4.5	$\sim 6 \times 10^{-12}$	$< 10^{-6}$	> 11
2	0	37.5	10.5	A	6	—	—	—
3	4.08×10^5	45.0	10.0	B	11.5	5.8×10^{-12}	4.5×10^{-7}	11.6
4	1.58×10^5	52.5	12.5	B	4.5	$\sim 6 \times 10^{-12}$	$< 10^{-6}$	> 11
5	3.81×10^5	39.2	14.4	B	6	$\sim 6 \times 10^{-12}$	$< 10^{-6}$	> 11
6	0	39.0	13.0	B	7	—	—	—
7	0	40.0	14.0	C	3	—	—	—
8	5.68×10^5	39.6	10.8	C	6	6.5×10^{-12}	2.5×10^{-7}	12.0
9	0	39.8	11.2	C	2	—	—	—
10	0	42.2	11.3	D	1	—	—	—
11	2.25×10^5	38.9	12.6	D	4.5	6.1×10^{-12}	6.0×10^{-7}	11.4

has calculated the number of effective triple collisions in a mixture of perfect gases for the case where molecules of kinds (1) and (3) will react if they come within a distance δ of a molecule of kind (2). The result is

$$Z = 8\sqrt{2}\pi^{\frac{1}{2}}N_1N_2N_3\sigma_{12}^2\sigma_{23}^2\delta(kT)^{\frac{1}{2}}\left(\frac{1}{(\mu_{23})^{\frac{1}{2}}} + \frac{1}{(\mu_{12})^{\frac{1}{2}}}\right),$$

where the N 's refer to the number of molecules per cc of each type, the σ 's to the average molecular diameters, and the μ 's to the reduced masses. It follows from this that the reaction $H+H+M$ should be $\sqrt{2}$ times faster than $D+D+M$,¹² the result being the same for an atomic or a molecular third body. Hence for deuterium atoms we will assume

$$K_1 = (3.4 \times 10^{16})/1.41 = 2.4 \times 10^{16}.$$

We thus have the necessary data to calculate the stationary D atom concentration and the collision efficiency of reaction (3). If α is the fraction of CH_4 reacting per second, then

$$[D] = \left(\frac{(2I_{\text{abs.}}/N) - \alpha[CH_4]}{K_1[M]} \right)^{\frac{1}{2}},$$

and the collision yield of reaction (3) is

$$\alpha/b[D],$$

where b is a collision factor having the value 3.0×10^{14} sec.⁻¹ mole⁻¹ cm³. This is calculated assuming the diameter of the methane molecule to be 3.75×10^{-8} cm.

In calculating E from the collision yield a steric factor of 0.1 has been assumed in conformity with the usual practice. The back reaction has been neglected, since its effect is negligible at small percentage conversions.

On account of the analytical difficulties previously mentioned, the data for runs 1 to 6 are merely qualitative. Nevertheless they serve to set a lower limit for the activation energy. For, even if the blank correction were omitted entirely, values of approximately 11 Kcal. would be obtained. In the last runs, where the blank corrections are smaller, a measurable exchange

is established, and we obtain more definite values for the activation energy.

Preliminary measurements have also been made with ethane and deuterium. These indicate, in agreement with the results of the first section, that the activation energy of the reaction is much lower than that of the reaction with methane.

DISCUSSION

(a) The reaction between deuterium atoms and methane

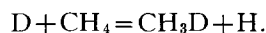
Our results indicate a value of 11.7 Kcal. for the photosensitized reaction. This is in complete agreement with the value of >11 Kcal. previously found by Geib and one of us by the discharge tube method.

Recently Farkas¹³ has investigated the thermal reaction between deuterium atoms and ammonia. He finds an activation energy of 11 ± 1 Kcal. At 1000°K his rate for D atoms and methane in some preliminary experiments is 6 times that for ammonia. Hence the activation energy must be almost the same, since there is no reason to assume a very different steric factor. His results are therefore in agreement with our findings.

It must therefore be concluded that the value of about 5 Kcal. reported by Taylor, Morikawa, and Benedict³ is much too low. In the absence of a detailed account of their work, we are unable to suggest any explanation of the discrepancy.

Farkas finds a different order of reactivity for the series $D+NH_3$, H_2O , CH_4 than was found previously by Geib and one of us. This, however, is obviously due to the fact that, as we pointed out, some wall effects were undoubtedly occurring in the reactions with ammonia and water. These thus appeared somewhat faster than the methane reaction, whereas Farkas finds them to be somewhat slower. Our values of the activation energies, however, are in excellent agreement.

There seems to be no doubt that all these reactions proceed by a direct atomic metathesis analogous to the ortho-para hydrogen conversion, *viz.*

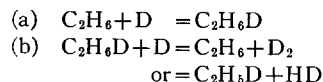
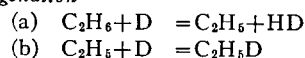
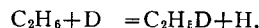


¹² This relation has been confirmed experimentally by Amdur (J. Am. Chem. Soc. 57, 856 (1935)), using a discharge tube method. He concluded, however, that atoms, not molecules, were the effective third bodies.

¹³ Farkas, J. Chem. Soc. 26 (1936).

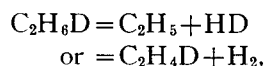
(b) The reaction between deuterium atoms and ethane

As we have shown, this reaction has a much lower activation energy, in the neighborhood of 6.3 Kcal. There are three main possibilities for the mechanism of the reaction:

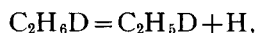
I. Hydrogenation*II. Dehydrogenation**III. Exchange by Metathesis*

Mechanism *III* is undoubtedly the correct one for the reactions of deuterium atoms with methane, ammonia, etc., as described above. However, in view of the fact that ethane and acetylene are known to have a strong "catalytic" effect in destroying hydrogen atoms,⁶ some other mechanism must exist, since *III* regenerates one hydrogen atom for each one destroyed and hence cannot account for a catalytic recombination. Furthermore the activation energies of the reactions with ethane and acetylene are so much lower than those for methane, ammonia, and water that it is obvious that the mechanisms must be distinctly different.

Mechanism *I* is very unlikely, since *I* (a) would presumably have to occur at a triple collision. This would make the reaction far too slow to enable ethane to exert a strong catalytic effect on the recombination of hydrogen atoms. Furthermore, even if *I* (a) occurred sufficiently rapidly, the very unstable molecule $\text{C}_2\text{H}_6\text{D}$ would have little chance of surviving long enough (10^{-6} sec.) to meet a D atom and give *I* (b). Hence in general we would expect *I* (a) to be followed by

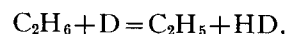


which would make the whole process indistinguishable from *II* (a), or else by

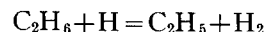


which would give a result indistinguishable from *III*.

Hence we must conclude that *II* is the correct mechanism, and that the measured heat of activation (6.3 Kcal.) is that of the reaction



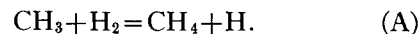
and hence the companion reaction



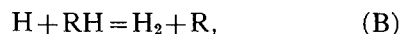
also has an activation energy of the same order of magnitude.

The activation energy of the latter reaction is of very considerable importance from the point of view of the mechanism of the decomposition of gaseous organic compounds. The Rice free radical theory¹⁴ has given a very satisfactory explanation of the products of organic decompositions. The theory has been extended to first order reactions, and it has been suggested that the majority of these occur by chain mechanisms.¹⁵ These mechanisms are very attractive in principle, and they have received support from the fact that the introduction of free radicals into a vessel containing an organic substance may cause chains to be set up.¹⁶ This, however, merely shows that chains *can* be set up by free radicals, and does not prove that free radicals are present and actually do set up chains during the normal slow decomposition of the substances concerned.

Recently the work of Patat and Sachsse¹⁷ has thrown considerable doubt on the idea that most organic decompositions proceed by a radical chain mechanism. They measured the rate of the ortho-para hydrogen conversion in the presence of decomposing organic compounds, and were thus able to detect hydrogen atoms produced by the decomposition, or by the reaction



In general the hydrogen atoms produced in this way are being destroyed by the reaction



¹⁴ Rice and Rice, *The Aliphatic Free Radicals* (Baltimore, 1935).

¹⁵ Rice and Herzfeld, *J. Am. Chem. Soc.* **56**, 284 (1934).

¹⁶ Frey, *Ind. Eng. Chem.* **26**, 200 (1934); Allen and Sickman, *J. Am. Chem. Soc.* **56**, 1251, 2031 (1934); Leermakers, *ibid.* **56**, 1899 (1934).

¹⁷ Patat and Sachsse, *Nach. Ges. Wiss. Göttingen*, [III] **1**, 41 (1935); *Naturwiss.* **23**, 247 (1935); *Zeits. f. physik. Chemie* **B31**, 105 (1935); Sachsse, *ibid.* **B31** 79 (1935).

where RH is an organic molecule and R a free radical. Hence the stationary concentration of hydrogen atoms is defined by the two processes, and we get

$$\frac{[\text{CH}_3]}{[\text{H}]} \sim \frac{K_B[\text{RH}]}{K_A[\text{H}_2]}.$$

Having evaluated $[\text{H}]$ by means of the ortho-para hydrogen conversion, we can thus calculate $[\text{CH}_3]$ and compare it with the value calculated from the Rice-Herzfeld mechanism. In general, using the activation energies assigned to the above reactions by Rice and Herzfeld, Patat and Sachsse find the hydrogen atom concentrations to be several powers of 10 lower than those calculated from the free radical chain theory. Thus for the decomposition of ethane the Rice-Herzfeld mechanism is

	<i>E</i> , Kcal.
(1) $\text{C}_2\text{H}_6 = 2\text{CH}_3$	80
(2) $\text{CH}_3 + \text{C}_2\text{H}_6 = \text{CH}_4 + \text{C}_2\text{H}_5$	20
(3) $\text{C}_2\text{H}_5 = \text{C}_2\text{H}_4 + \text{H}$	49
(4) $\text{H} + \text{C}_2\text{H}_6 = \text{H}_2 + \text{C}_2\text{H}_5$	17
(5) $\text{H} + \text{H} = \text{H}_2$	Triple collision
(6) $\text{H} + \text{C}_2\text{H}_5 = \text{C}_2\text{H}_4 + \text{H}_2$ (or C_2H_6)	
(7) $\text{H} + \text{CH}_3 = \text{CH}_4$	small
(8) $\text{CH}_3 + \text{C}_2\text{H}_5 = \text{C}_3\text{H}_8$	8
(9) $2\text{C}_2\text{H}_5 = \text{C}_4\text{H}_{10}$	8

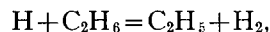
If reactions (5), (7), (8) and (9) are assumed to be negligible, this gives a first order rate and good agreement with the observed value of the activation energy. Furthermore we obtain approximately

$$\frac{[\text{CH}_3]}{[\text{H}]} = \frac{K_4[\text{C}_2\text{H}_6]}{K_A[\text{H}_2]}.$$

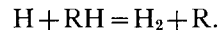
Patat and Sachsse found, using $K_4 = 17$ Kcal. as given by Rice and Herzfeld, that the observed hydrogen atom concentration is about 1000 times too small.

Now, as pointed out above, the present investigation indicates that the activation energy

of reaction (4) is about 6 Kcal. instead of 17 Kcal. There are also theoretical grounds for believing that 17 Kcal. is much too high.¹⁸ If we calculate $[\text{H}]$ using 6 Kcal. for this reaction, then the value obtained agrees almost exactly with that found by Patat and Sachsse. It thus appears that if we accept the value of 6 Kcal. found by us as being the activation energy of the reaction



then the objections to the free radical scheme from the point of view of the stationary hydrogen atom concentration no longer hold. The same is true for most of the other free radical chain mechanisms if we assume that all the Rice-Herzfeld activation energies are too high for reactions of the type



Such a change in the activation energy of reaction (4), however, seems to introduce insurmountable difficulties into the application of the scheme to first order reactions. Thus in the case of ethane the fundamental reactions are (1), (2), (3) and (4), and these cannot be altered without virtually abandoning the entire free radical theory. As we have seen the change in E_4 brings the results into line with the work of Patat and Sachsse as far as the stationary hydrogen atom concentration is concerned. The overall order of the reaction and the theoretical value of E , however, are largely dependent on the manner in which the chains are terminated. The change in E_4 by altering the relative concentrations of the reacting substances upsets the relationships between the rate constants and it is no longer permissible to neglect reactions (8) and (9). Under these circumstances the scheme no longer predicts a first order rate or the correct value of the overall activation energy.

¹⁸ London, Zeits. f. Elektrochem. **35**, 552 (1929).