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## The Reaction of Hydrogen Atoms with the Paraffin Hydrocarbons\*

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The reactions of atomic hydrogen produced by a discharge with ethane, propane, and neo-pentane have been investigated. All three reactions proceed at approximately the same rate, with activation energies of *ca.* 9 kcal., assuming a steric factor of 0.1. It is suggested, however, that the activation energies are in reality somewhat lower than this, with correspondingly smaller steric factors.

In the reaction with neo-pentane considerable ethane is produced. When deuterium atoms are used, this ethane is found to be only slightly exchanged. It is concluded, therefore, that ethane cannot arise by recombination of radicals, and must be formed in one step, presumably from an excited neo-pentane molecule.

### INTRODUCTION

THE reactions of atomic hydrogen with the paraffin hydrocarbons are of considerable importance in the mechanism of a variety of thermal and photo-chemical reactions. On the basis of a review of previous work it was concluded<sup>1</sup> that the "best" values of the activation energies (assuming a steric factor of 0.1) of these reactions were:

$H + CH_4$	$13 \pm 2$ kcal.
$H + C_2H_6$	$6.7 \pm 1$ kcal.
$H + C_3H_8$	$10 \pm 2$ kcal.
$H + n-C_4H_{10}$	$10 \pm 1.5$ kcal.
$H + iso-C_4H_{10}$	$10 \pm 1.5$ kcal.

These activation energies have, for the most part, been calculated from the collision yield of the reaction at room temperature, and are thus largely merely a measure of the relative rates of the reactions at room temperature. However, there seems to be no doubt that the position of ethane in the series is anomalous. It was therefore considered that it would be of value to repeat the work with ethane and propane under identical conditions.

Also, since neo-pentane is surprisingly inert to mercury photosensitization<sup>2</sup> at room temperature, an investigation has been made of its reaction with H atoms.

### EXPERIMENTAL

Atomic hydrogen was produced by the discharge-tube method in an apparatus similar to that previously described.<sup>3</sup> Methane and other products were separated from the hydrogen stream by means of a silica-gel trap cooled with liquid air. The products were then further analyzed by a modification of the Ward fractionation method.<sup>4</sup> Final identifications and quantitative determinations were done by combustion analysis of the individual fractions.

The H atom concentrations were measured during each run by means of two Wrede gauges,<sup>5</sup> one placed where the atom stream entered the reactor, and the other at the bottom of the vessel.<sup>3</sup> The concentration used in the calculation of collision yields was the average of the two values. The atom concentration was varied by varying the current through the discharge.

Collision yields were calculated in the usual way, a steric factor of 0.1 being assumed. Molecular diameters were taken as<sup>6</sup> 2.1 Å for H, 3.7 for  $C_2H_6$ , 4.2 for  $C_3H_8$ , and a value of 5.0 was assumed for neo-pentane.

Ethane was purified by photo-bromination followed by fractional distillation. Propane was purified by fractional distillation. Neo-pentane was purified by the destruction of impurities by

\* Contribution No. 1625 from the National Research Council, Ottawa, Canada.

<sup>1</sup> E. W. R. Steacie, *Atomic and Free Radical Reactions* (Reinhold Publishing Corporation, New York, 1946), p. 289.

<sup>2</sup> B. deB. Darwent and E. W. R. Steacie, *J. Chem. Phys.* (in press).

<sup>3</sup> G. M. Harris and E. W. R. Steacie, *J. Chem. Phys.* **13**, 554 (1945).

<sup>4</sup> J. J. Savelli, W. D. Seyfried, and B. M. Filbert, *Ind. Eng. Chem. Anal. Ed.* **13**, 868 (1941).

<sup>5</sup> E. Wrede, *Zeits. f. Physik* **54**, 53 (1929); P. Hartek, *Zeits. f. physik. Chemie* **A139**, 98 (1928).

<sup>6</sup> K. F. Bonhoeffer and P. Hartek, *Photochemie* (Theodor Steinkopff, Verlag, Leipzig, 1933); T. Titani, *Bull. Inst. Phys. Chem. Res. (Japan)* **8**, 433 (1929).

TABLE I. Reaction of H and D atoms with paraffins; temperature  $24 \pm 2^\circ\text{C}$ , reaction time 0.72 sec.

Run no.	Atomic reactant	Hydrocarbon reactant	Partial pressure, mm			Percent reaction	Collision yield $\times 10^4$	Activation energy, kcal. (assuming $s = 0.1$ )
			H <sub>2</sub>	H	paraffin			
1	Hydrogen	Ethane	0.30	0.051	0.019	0.68	0.83	9.5
2	Hydrogen	Ethane	0.31	0.050	0.0009	1.20	1.5	9.2
3	Hydrogen	Ethane	0.36	0.022	0.0068	0.55	1.5	9.1
4	Hydrogen	Ethane	0.33	0.024	0.013	0.75	2.0	9.0
5	Deuterium	Ethane	0.27	0.063	0.021	3.1	3.0	8.7
6	Deuterium	Ethane	0.28	0.065	0.011	3.1	2.9	8.8
7	Hydrogen	Propane	0.32	0.027	0.0048	3.9	6.0	8.5
8	Hydrogen	Propane	0.33	0.028	0.0073	4.0	5.6	8.4
9	Hydrogen	Neo-pentane	0.31	0.020	0.0040	0.8	1.7	9.3
10	Hydrogen	Neo-pentane	0.31	0.077	0.0080	3.9	2.1	9.1
11	Hydrogen	Neo-pentane	0.31	0.070	0.0065	4.3	2.6	9.0
12	Hydrogen	Neo-pentane	0.29	0.037	0.011	1.0	1.2	9.3
13	Hydrogen	Neo-pentane	0.27	0.042	0.0031	1.7	1.7	9.2
14	Deuterium	Neo-pentane	0.26	0.075	0.0090	3.1	1.8	9.2
15	Deuterium	Neo-pentane	0.29	0.032	0.010	—	—	—

mercury photosensitization.<sup>2</sup> None of the gases contained any impurity detectable by the analytical methods used. A mass spectrometric analysis of neo-pentane showed it to be better than 99 percent pure.\*\*

Hydrogen was taken from a commercial cylinder and purified in the usual way. Deuterium was obtained in cylinders from the Stuart Oxygen Company.

### RESULTS

The results of all experiments are given in Table I.

### Products

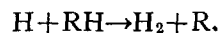
With ethane the only detectable product was methane, in agreement with previous work. With propane methane was the main product, but, in addition, a very small amount of ethane was formed (approximately 0.5 percent of the propane consumed formed ethane). With neo-

pentane substantial amounts of ethane were formed. The products from neo-pentane are given in Table II.

In experiments with deuterium, the hydrocarbon fractions were burned to water and sealed off in bulbs. These were later converted to hydrogen on a hot tungsten filament, and their deuterium content determined with a mass spectrometer. We are greatly indebted to Professor H. G. Thode and Messrs. C. B. Collins, J. G. Lindsay, and E. G. Roth of McMaster University for these analyses. The results are given in Table III.

### DISCUSSION

From Table I it will be seen that ethane reacts at a rate similar to that of propane, but slightly less. Previous data led to a rather different conclusion. However, if previous results are recalculated using the same assumptions as to mechanism, etc., it is found that all present data are in substantial agreement. The results of various workers at room temperature are compared in Table IV. These have all been recalculated from the original data on the assumption that the rate-determining step is the reaction



It may therefore be concluded that the results obtained at room temperature, assuming a steric factor of 0.1, lead to the following values of the activation energy:

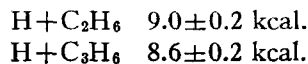


TABLE II. Products of the reaction of H atoms with neo-pentane.

Run no.	Partial pressure of H atoms, mm	Products expressed as moles per 100 moles of neo-pentane passed through the system		CH <sub>4</sub> C <sub>2</sub> H <sub>6</sub>
		methane	ethane	
9	0.020	3.3	0.3	11
10	0.077	11.4	4.0	2.8
11	0.070	12.5	4.6	2.7
12	0.037	4.8	0.3	16
13	0.042	5.9	1.2	5
14	0.075*	15	0.3	—

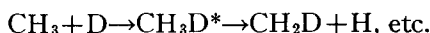
\* D atoms.

\*\* We are indebted to Dr. F. L. Mohler of the National Bureau of Standards, Washington, for this analysis.

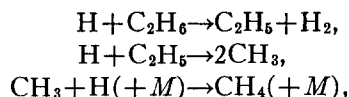
Actually, of course, these results are equally compatible with lower activation energies and correspondingly lower steric factors. We have recently discussed the evidence for all the paraffins in some detail,<sup>7</sup> and conclude that the steric factors for these reactions are probably much lower than has been previously assumed. In any case, however it may be unambiguously stated that there is little difference in the collision yields of the two reactions, and ethane thus no longer occupies an anomalous position in the series of paraffins, and is slightly less reactive than propane.

The fact that the rates of the reaction of H atoms with ethane and neo-pentane are identical is in line with the results of Smith and Taylor<sup>8</sup> for the reaction of methyl radicals with these substances.

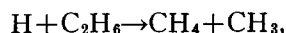
In the case of ethane the results of deuterium atom experiments given in Table III show that methane formed from ethane is highly deuterized while "unreacted" ethane is deuterized only to the extent of about 9 percent. The methane results are in line with previous work on ethane<sup>9</sup> and propane,<sup>10</sup> and there is little doubt that the observed exchange is due to the exchange of methyl radicals by the mechanism



The small deuterization of ethane indicates that recombination of radicals to form ethane is not of much importance, since ethyl radicals, as well as methyl, are readily exchanged.<sup>10</sup> The results are thus in agreement with the generally accepted mechanism of the reaction, *viz.*,



with other recombination reactions occurring only to a minor extent. It may be noted that the very high deuterization of methane definitely rules out the possible primary step



<sup>7</sup> E. W. R. Steacie, B. deB. Darwent, and W. R. Trost, *Trans. Faraday Soc.* (in press).

<sup>8</sup> J. O. Smith and H. S. Taylor, *J. Chem. Phys.* **7**, 390 (1939).

<sup>9</sup> N. R. Trenner, K. Morikawa, and H. S. Taylor, *J. Chem. Phys.* **5**, 203 (1937).

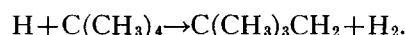
<sup>10</sup> E. W. R. Steacie and N. A. D. Parlee, *Trans. Faraday Soc.* **35**, 854 (1939).

TABLE III. Products from runs with deuterium.

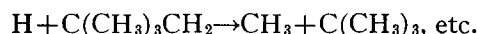
Run no.	Reactants	Product	$\frac{\text{D}}{\text{D}+\text{H}} \times 100$ in product
—	Deuterium supply		85.5 ± 2
5	D + C <sub>2</sub> H <sub>6</sub>	methane	74 ± 2
6	D + C <sub>2</sub> H <sub>6</sub>	methane	65.5 ± 2
6	D + C <sub>2</sub> H <sub>6</sub>	ethane	8.8 ± 1
14	D + C <sub>5</sub> H <sub>12</sub>	methane	80.5 ± 2
14	D + C <sub>5</sub> H <sub>12</sub>	Combined products other than methane	8.8 ± 1
15	D + C <sub>5</sub> H <sub>12</sub>	C <sub>2</sub> fraction	4 ± 1
15	D + C <sub>5</sub> H <sub>12</sub>	C <sub>4</sub> fraction	10 ± 1
15	D + C <sub>5</sub> H <sub>12</sub>	"unreacted" neo-pentane	1.5 ± 0.5

since this could lead at most to 50 percent exchange of the hydrogen in the resulting methane.

An unusual feature of the reaction of H atoms with neo-pentane is the comparatively high yield of ethane. It appears from the data of Table II that the ethane yield increases with increasing H atom concentration. It seems almost certain that the initial step, as with other paraffins, is the reaction



It would be expected that this would be followed by atomic cracking reactions of the type



This type of mechanism accounts readily for the high yield of methane, but it is difficult to see why ethane should be an important product here and be almost negligible in the case of propane.

The results of Table III show that in runs with deuterium the methane is virtually com-

TABLE IV. Comparison of the results of various observers on the reaction of H atoms with ethane and propane at 25°C.

Investigation	Reaction	Collision yield $\times 10^8$	E, kcal., assuming $s = 0.1$
Chadwell and Titani*	H + C <sub>2</sub> H <sub>6</sub>	1.8	9.2
Steacie**	H + C <sub>2</sub> H <sub>6</sub>	3.3	8.8
This paper	H + C <sub>2</sub> H <sub>6</sub>	2.0	9.0
Taylor <i>et al.</i> ***	D + C <sub>2</sub> H <sub>6</sub>	6.2	8.5
This paper	D + C <sub>2</sub> H <sub>6</sub>	3.0	8.7
Steacie and Parlee†	H + C <sub>3</sub> H <sub>8</sub>	5.8	8.7
Taylor <i>et al.</i> ***	H + C <sub>3</sub> H <sub>8</sub>	0.9	9.5
This paper	H + C <sub>3</sub> H <sub>8</sub>	6.0	8.6

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

\*\* E. W. R. Steacie, *J. Chem. Phys.* **6**, 37 (1938).

\*\*\* See reference 9.

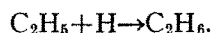
† See reference 10.

pletely exchanged. This is in line with the results for other paraffins, and proves that methane is formed via methyl radicals. The "unreacted" neo-pentane is not appreciably exchanged, and hence recombination of radicals to reform neo-pentane does not occur.

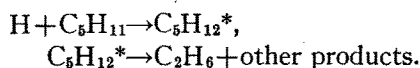
The other products, and particularly the  $C_2$  fraction, are only slightly exchanged. Ethane cannot, therefore, have arisen via  $CH_3$ , or  $C_2H_5$ , i.e., by the reactions



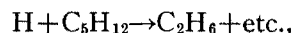
or



The only reasonable alternative appears to be that it arises in one step from a reaction of neo-pentane or neo-pentyl. The most likely reaction of this type appears to be



Offhand this appears to violate the ideas of Rice and Teller.<sup>11</sup> However, it seems to us that there is a very distinct difference between the postulation of reactions of the type



which are definitely contrary to the Principle of Least Motion, and of



In the latter case an excited molecule is formed which may be expected to have a relatively long life. It is therefore similar to an ordinary neo-pentane molecule which has been activated thermally and can undergo decomposition by a molecular rearrangement in the ordinary way.

The authors wish to express their indebtedness to Dr. B. deB. Darwent for many suggestions and discussions.

<sup>11</sup> F. O. Rice and E. Teller, *J. Chem. Phys.* **6**, 489 (1938).

## Dielectric Measurement of Liquids at Microwave Frequencies\*

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(Received December 17, 1947)

A method of measuring the dielectric properties of medium and high loss liquids at microwave frequencies is described. In this method the liquid sample is placed in an open circuit-terminated section of wave-guide and standing wave-ratios are measured at intervals as the length of the dielectric liquid column in the wave guide is changed. The method of measuring the wave-length of the radiation in the liquid-filled wave guide is indicated. A simple procedure for calculating the dielectric properties from these measurements is presented. Some dielectric properties of liquids measured with this method at 3-cm wave-length are given.

### I. INTRODUCTION

**D**IELECTRIC measurements have been made for more than half a century by investigators who were either interested in studying molecular structure or appraising materials to be used in electric installations. No single method

of measuring the dielectric constant and power factor of a substance has been found that could be applied at all frequencies, so it is necessary to employ different methods if one wishes to investigate the dielectric properties of a material over all available frequency ranges. Moreover, at a single frequency it is sometimes necessary to employ different methods, determined by the power factor of the material being investigated, so that the methods that have been and are being employed for dielectric measurements, are numerous indeed. At certain frequencies there are

\* This paper is based upon work performed at Princeton University through support extended jointly by the Navy Department (Bureau of Ships) and the Signal Corps, U. S. Army under Contract No. W-36-039-sc-32011, File No. 10478-PH-46-91(SCEI). The information contained herein has appeared in Technical Report No. 7 of the Princeton University Plastics Laboratory.