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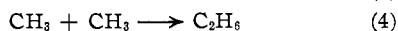
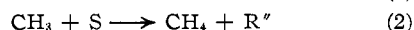
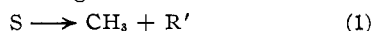
The Relative Activation Energies of Removal of Primary, Secondary and Tertiary Hydrogen Atoms by Methyl Radicals¹

BY FRANCIS OWEN RICE AND THOMAS A. VANDERSLICE

RECEIVED JULY 15, 1957

We have decomposed $\text{CH}_3\text{N}=\text{NCH}_3$ in presence of a large excess of the following hydrocarbons, CH_3CD_3 , $\text{CH}_3\text{CD}_2\text{CH}_3$ and $(\text{CH}_3)_3\text{CD}$ and have determined by mass spectrometric analysis the $[\text{CH}_4]/[\text{CH}_3\text{D}]$ ratios in each case at a series of temperatures. From the results we calculated the following differences in activation energy (ΔE) for the removal of hydrogen atoms by methyl radicals: primary deuterium — primary hydrogen, 0.6 kcal.; primary hydrogen — secondary hydrogen, 2.3 kcal.; primary hydrogen — tertiary hydrogen, 2.9 kcal. The purpose of this research was the determination, by a rather direct means, of the difference in activation energy for the removal of a primary hydrogen atom and a primary deuterium atom and also the difference in activation energy for the removal of a primary hydrogen atom, a secondary hydrogen atom and a tertiary hydrogen atom by a methyl radical.

Previous work was usually based upon a study of two reactions occurring in the same system.² For example, when a source of methyl radicals (S) is decomposed in the presence of a hydrocarbon containing only primary hydrogen atoms, we have these reactions occurring



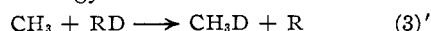
Then, the rate of formation of methane, R_{CH_4} , is given by

$$R_{\text{CH}_4} = k_2[\text{CH}_3][\text{S}] + k_3[\text{CH}_3][\text{RH}]$$

However, the direct determination of $[\text{CH}_3]$ is almost always impossible. It is therefore necessary to determine the ratio of rates

$$\frac{R_{\text{CH}_4}}{\sqrt{R_{\text{C}_2\text{H}_6}}} = \frac{k_2[\text{S}]}{\sqrt{k_4}} + \frac{k_3[\text{RH}]}{\sqrt{k_4}}$$

The first term on the right side is determined from experiments in the absence of hydrocarbon and hence $E_3 - \frac{1}{2}E_4$ may be found. The activation energy for reaction 4 is taken to be zero and thus the measurements give the value of E_3 . If the analogous reaction is carried out using a completely deuterated hydrocarbon, it is possible to measure the activation energy of the reaction



The difference is small and to determine it requires three separate experiments, one in the absence of hydrocarbon, another in the presence of hydrocarbon and the third in the presence of a deuterated hydrocarbon.

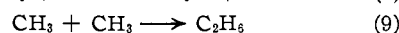
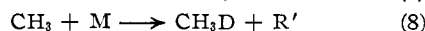
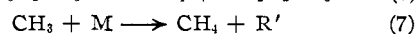
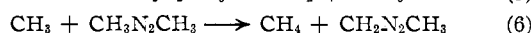
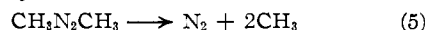
It is definitely known^{2b} that the activation energy for the reaction of methyl radicals with primary hydrogen atoms in paraffin hydrocarbons is greater than that with secondary hydrogen atoms, and the reaction with secondary hydrogen atoms has a greater activation energy than with tertiary hydrogen atoms. When the hydrocarbon used in these experiments contains both primary and secondary hydrogen atoms, the value for the activation energy

(1) This work was supported in part by the Petroleum Research Corp. fund.

(2) (a) P. Ausloos and E. W. R. Steacie, *Can. J. Chem.*, **33**, 31 (1955); (b) A. F. Trotman-Dickenson and E. W. R. Steacie, *J. Phys. Colloid Chem.*, **55**, 908 (1951); (c) M. H. Jones and E. W. R. Steacie, *Can. J. Chem.*, **31**, 505 (1953); (d) A. F. Trotman-Dickenson, J. R. Birchard and E. W. R. Steacie, *J. Chem. Phys.*, **19**, 163 (1951); (e) E. Whittle and E. W. R. Steacie, *ibid.*, **21**, 993 (1953).

will be a measure of the removal of the secondary hydrogen atom and also, in part, the primary hydrogen atoms. The value found for butane, for example,³ will be slightly higher than the real value for the secondary hydrogen atom since at each temperature some primary hydrogen will be reacting. The same would be true for the determination of the activation energy for the removal of a tertiary hydrogen atom by a methyl radical since some primary hydrogens would still react at all temperatures. This effect would be smaller with the tertiary hydrogen case than with the secondary hydrogen case since the activation energy difference between a primary and a secondary hydrogen atom is less than that between a primary hydrogen and a tertiary hydrogen atom. This intrinsic error would increase with temperature.

It was felt that a more accurate method using a low percentage of methyl radical source could be developed. The general reaction scheme for this pyrolytic study is



where M is a hydrocarbon containing both hydrogen and deuterium atoms. The thermal and photolytic decompositions of azomethane and its use as a source of methyl radicals have been widely studied.⁴ The evidence overwhelmingly indicates that the decomposition 5 proceeds by a free radical mechanism with an activation energy of approximately 53 kcal.^{5,6}

Writing out the rate expressions for the above reactions where R_{CH_4} and $R_{\text{CH}_3\text{D}}$ are the rates of production of CH_4 and CH_3D , respectively, we have

$$R_{\text{CH}_4} = k_6[\text{CH}_3][\text{CH}_3\text{N}_2\text{CH}_3] + k_7[\text{CH}_3][\text{M}]$$

$$R_{\text{CH}_3\text{D}} = k_8[\text{CH}_3][\text{M}]$$

From these equations it follows that

$$\frac{R_{\text{CH}_4}}{R_{\text{CH}_3\text{D}}} = \frac{k_7}{k_8} + \frac{k_6[\text{CH}_3\text{N}_2\text{CH}_3]}{k_8[\text{M}]}$$

(3) J. O. Smith and H. S. Taylor, *ibid.*, **7**, 390 (1939).

(4) "Atomic and Free Radical Reactions," E. W. R. Steacie, Reinhold Publ. Corp., New York, N. Y., 1954.

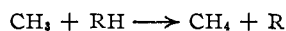
(5) H. Austin Taylor and Francis P. Jahn, *J. Chem. Phys.*, **7**, 470 (1939).

(6) F. O. Rice and B. L. Evering, *THIS JOURNAL*, **55**, 3898 (1933).

If reaction 6 could be neglected, a measure of the $[\text{CH}_4]/[\text{CH}_3\text{D}]$ ratio at various temperatures would give the difference in activation energy between reactions 7 and 8.

As Jones and Steacie have shown,⁷ the hydrogen atoms in hydrocarbons are somewhat more difficult to remove than the hydrogen atoms in azomethane, and hence it must be present in very small amounts in order to be able to neglect reaction 2.

A pyrolytic source has the disadvantage that the initial step has an activation energy of more than four times that of the reaction which is being



studied. This means that the work must be done at high enough temperatures to decompose the azomethane appreciably but not at temperatures high enough to decompose the hydrocarbon except by sensitization by methyl radicals from the source. This temperature restriction, however, is not a prohibitive one.

In the present study, M represents CH_3CD_3 , $\text{CH}_3\text{CD}_2\text{CH}_3$ and $(\text{CH}_3)_3\text{CD}$. By this method the use of the first compound would give directly the difference in activation energy between the removal of a primary hydrogen atom and a primary deuterium atom. The second would give the difference in activation energy between the removal of a primary hydrogen atom and a secondary deuterium atom. The last would give the difference in activation energy for the removal of a primary hydrogen atom and a tertiary deuterium atom. If the assumption is made that the difference in activation energy between the removal of a hydrogen atom and a deuterium atom is independent of whether they are both primary, both secondary or both tertiary, these measurements give the difference between a primary hydrogen and a tertiary hydrogen atom. This assumption appears to be plausible.

McNesby and his co-workers⁸ employed a method similar to the one employed in this work. Using a 50-50 mixture of CH_3COCH_3 and $\text{CD}_3\text{-COCD}_3$ at temperatures from 466 to 525°, they studied the reactions of CD_3 and CH_3 radicals produced by measuring the rate of formation of $[\text{CH}_4]/[\text{CH}_3\text{D}]$ and $[\text{CD}_3\text{H}]/[\text{CD}_4]$. The later results gave a good straight line for the Arrhenius plot but the $[\text{CH}_4]/[\text{CH}_3\text{D}]$ ratio gave a somewhat scattered Arrhenius plot.

Experimental

The apparatus used in this investigation was a conventional static system for the study of reaction kinetics. A 60-cc. reaction vessel was made from a 25 mm. quartz tube fitted with a 5 mm. thermocouple well and was thoroughly carbonized before use. The reaction vessel was connected to the gas handling apparatus by a 3 mm. graded seal. The pressure measurements were made with a 1 mm. capillary manometer. The reaction vessel was placed inside a three inch aluminum rod bored out to accommodate the quartz vessel. Surrounding the aluminum rod was an aluminum core wound at one-eighth inch intervals with B & S #12 nichrome wire. Two inches of "Fiberfrax" insulation together with the transit pipe surrounding the furnace sufficed for thermal insulation. In making up a standard mixture, measured amounts of the substrate gas and azo-

(7) M. H. Jones and E. W. R. Steacie, *J. Chem. Phys.*, **21**, 1018 (1953).

(8) J. R. McNesby, T. W. Davis and Alvin S. Gordon, *THIS JOURNAL*, **76**, 823, 1416 (1954).

methane were thoroughly mixed by the Toepler pump and allowed to stand overnight.

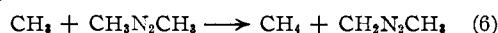
Temperature measurement was made by means of an iron constantan thermocouple calibrated by the Bureau of Standards, Washington, D. C., at sufficient points so that the temperature could be read at any point in the interval to within 0.1°. A Leeds and Northrup K-2 potentiometer was used to measure the e.m.f. of the thermocouple. Every precaution was used with regard to circuit construction to ensure that the temperature could actually be measured to the desired accuracy. A description of the electronic controller used in the study is given elsewhere.

Mass spectrometric analyses were made using a modified Westinghouse sector field instrument with a 90° tube. The ion currents were recorded on a Leeds and Northrup Speedomax Type C recorder. The methanes were distilled off at liquid nitrogen temperature in order to eliminate the unreacted azomethane and substrate. Several experiments with known mixtures of methanes verified that there was no fractionation at these temperatures. This agrees with work done by McNesby and his co-workers.⁸ The instrument was calibrated with purified Phillips research grade methane and a sample of CH_3D obtained from Dr. Plyler of the Bureau of Standards. Excellent agreement was obtained with patterns published elsewhere.¹⁰ The samples of standard gases were run at frequent intervals to ensure that the sensitivities and patterns did not change appreciably.

The azomethane was prepared by a modification of the method of Jahn.¹¹ The CH_3CD_3 and $\text{CH}_3\text{CD}_2\text{CH}_3$ were prepared by a published method.¹⁰ The purities, after low temperature distillation, were greater than 98%. The $(\text{CH}_3)_3\text{CD}$ was graciously supplied to us by C. D. Wagner of the Shell Development Company.¹²

Discussion

In this work a direct determination of the relative yields of CH_4 and CH_3D has been made for methyl radical sensitized reactions with various hydrocarbons containing both hydrogen and deuterium atoms. Studies have also been made on the effect of varying the concentration of the azomethane source which contributes to the methane production by the reaction



The presence of 5% azomethane changes the apparent difference in activation energy ($E_7 - E_8$) by less than 0.3 kcal. With 1% azomethane as a source it changes it by less than 0.1 kcal. Hence, using only 1% azomethane as a source of methyl radicals less than 0.1 kcal. error is introduced in the measurement of activation energies. Consequently a 1% concentration of azomethane was used in all further experiments. Further evidence that reaction 6 introduces no appreciable error is that the ratio of $[\text{CH}_4]$ to $[\text{CH}_3\text{D}]$ is independent of the per cent. decomposition of the 1% azomethane concentration. That is, the reaction can be allowed to proceed to 25, 50, 75% decomposition of azomethane and the ratio of $[\text{CH}_4]$ to $[\text{CH}_3\text{D}]$ is constant within the small experimental error.

The time of the various runs was 30 minutes. With each reaction, runs were made to show that the $[\text{CH}_4]/[\text{CH}_3\text{D}]$ ratio was independent of time and pressure. This appears to support the view that the products of the reaction do not change the ratio of $[\text{CH}_4]$ to $[\text{CH}_3\text{D}]$ by any significant amount. No significant amounts of H_2 , D_2 or HD

(9) To be published.

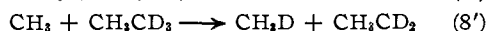
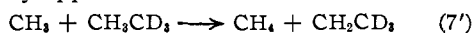
(10) D. O. Schissler, S. O. Thompson and J. Turkevich, *Disc. Faraday Soc.*, No. 10, 46 (1951).

(11) F. P. Jahn, *THIS JOURNAL*, **59**, 1761 (1937).

(12) ADI document #3029, Auxiliary Publication Project, Library of Congress, Washington, D. C.

were found with reactions involving CH_3CD_3 and $\text{CH}_3\text{CD}_2\text{CH}_3$ and very small amounts of H_2 and HD were found with $(\text{CH}_3)_3\text{CD}$. There were no significant 18 or 19 peaks in any of the reactions.

In the reaction scheme with CH_3CD_3 only the following reactions contribute to the CH_4 and CH_3D yield in any appreciable amount



Then

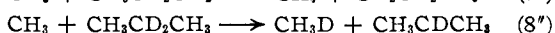
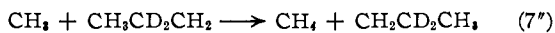
$$\frac{R_{\text{CH}_4}}{R_{\text{CH}_3\text{D}}} = \frac{k_7'[\text{CH}_3][\text{CH}_3\text{CD}_3]}{k_8'[\text{CH}_3][\text{CH}_3\text{CD}_3]} = \frac{k_7'}{k_8'} = \frac{[\text{CH}_4]}{[\text{CH}_3\text{D}]}$$

and a determination of this ratio at various temperatures gives the difference in activation energy between the removal of a primary hydrogen atom and a primary deuterium atom. $E_D - E_H$ was found to be 0.6 kcal. The standard deviation using a least squares plot was ± 0.04 kcal.

TABLE I
DATA FOR 1% AZOMETHANE PLUS 99% CH_3CD_3

Temp., °C.	$[\text{CH}_4]/[\text{CH}_3\text{D}]$
327.6	3.488
342.5	3.432
364.8	3.404
379.2	3.337
401.3	3.330
423.7	3.245

In the reaction scheme with $\text{CH}_3\text{CD}_2\text{CH}_3$ the reactions occur



Then

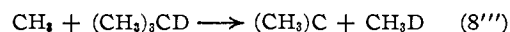
$$\frac{R_{\text{CH}_4}}{R_{\text{CH}_3\text{D}}} = \frac{k_7''}{k_8''} = \frac{[\text{CH}_4]}{[\text{CH}_3\text{D}]}$$

and a determination of this ratio at various temperatures gives the difference in activation energy between the removal of a primary hydrogen atom and a secondary deuterium atom. $E(\text{primary hydrogen}) - E(\text{secondary deuterium})$ is 1.7 kcal. The activation energy for removal of the secondary deuterium atom by a methyl radical is 0.6 kcal. higher than that of a secondary hydrogen atom under the assumption that the activation energy difference between a hydrogen atom and a deuterium atom is independent of whether they both are primary, both secondary or both tertiary. Hence the activation difference for removal of a primary hydrogen atom and a secondary hydrogen atom by a methyl radical is 2.3 kcal.

TABLE II

DATA FOR 1% AZOMETHANE PLUS 99% $\text{CH}_3\text{CD}_2\text{CH}_3$	
Temp., °C.	$[\text{CH}_4]/[\text{CH}_3\text{D}]$
312.1	3.095
333.6	3.395
356.8	3.488
377.6	3.650
400.0	3.921
421.0	3.942

In the case using 1% azomethane and 99% $(\text{CH}_3)_3\text{CD}$ the reactions occur



and the Arrhenius plot of $\ln \text{CH}_4/\text{CH}_3\text{D}$ versus $1/T$ gives the activation energy difference for removal of a primary hydrogen atom and a tertiary deuterium atom. This difference is found to be 2.3 kcal. and hence the activation energy difference for removal of a primary hydrogen atom and a tertiary hydrogen atom is 2.9 kcal.

TABLE III

DATA FOR 1% AZOMETHANE PLUS 99% $(\text{CH}_3)_3\text{CD}$			
Temp., °C.	$[\text{CH}_4]/[\text{CH}_3\text{D}]$	Temp., °C.	$[\text{CH}_4]/[\text{CH}_3\text{D}]$
305.3	1.438	372.5	1.790
322.5	1.545	386.9	1.824
334.4	1.552	401.8	1.848
359.4	1.699	416.7	1.960

The above results are in rather good agreement with the literature. The activation energy for the metathetical reactions of methyl radicals with ethane, butane and 2-methylpropane have been reported⁴ to be 10.4 ± 0.4 , 8.3 ± 0.2 and 7.6 ± 0.2 kcal., respectively. The work of Trotman-Dickenson, Birchard and Steacie gives the difference in activation energy between a primary and a secondary hydrogen atom on a hydrocarbon as 2.1 kcal. and the difference between a primary and tertiary hydrogen atom on a hydrocarbon as 2.8 kcal. Their experimental error is such that agreement with the present work may be fortuitous and, as Smith and Taylor pointed out,³ with the method they employed, differences in activation energy should be higher since some methyl radicals will remove primary hydrogen atoms when reacting with butane and also when reacting with 2-methylpropane even at the low temperatures generally employed in photolytic work. Nevertheless, the agreement is satisfactory.

WASHINGTON 17, D. C.