

THE REACTIONS OF METHYL RADICALS

By A. F. TROTMAN-DICKENSON, M.A., B.Sc., PH.D.
(I.C.I. RESEARCH FELLOW, UNIVERSITY OF MANCHESTER)

A LARGE proportion of contemporary research on reaction kinetics is devoted to the study of atomic and free-radical reactions both in the gas phase and in solution. There are many reasons for this. First, atomic and free-radical reactions are formally very simple; they are less influenced by their environment than are ionic reactions; they exemplify clearly the factors governing reactivity; they are often very symmetrical and are suitable for theoretical study; they may provide the avenue by which we shall arrive at a fuller understanding of the factors influencing the rates of reactions. Secondly, they are of extreme practical importance in the petroleum chemicals industry and in the production of high polymers. Thirdly, they are involved in many combustion and oxidation processes. Fourthly, they are relatively difficult to investigate and their study involves the use of many of the most advanced chemical techniques, so they provide a challenge to the worker in reaction kinetics.

Here we shall be concerned with the reactions of methyl radicals in the gas phase, which have been more fully investigated and are better understood than those of any other free radicals. As a result of intensive research in five or six laboratories during the last seven years we now have some quantitative knowledge of most types of methyl-radical reaction. Consequently, it is possible to write a fairly comprehensive review of these reactions in the expectation that new work will amplify what is written here and fill in the many gaps but that drastic revision will not be required. Here will be described the methods of research used in the study of methyl-radical reactions and the results so obtained, in the hope that this particular account may be a general guide to free-radical research in the gas phase. To this end the parallel behaviour of other radicals, which are much more difficult to investigate, will be referred to when this seems to be illuminating.

Early Work on Free Radicals.—The existence of short-lived alkyl free radicals was first demonstrated twenty years ago by Paneth and his co-workers. In the subsequent decade investigators were primarily concerned in detecting the presence of free radicals in reacting systems. Paneth showed that when organic vapours were passed through a furnace at a convenient temperature and over a metallic mirror, the mirror was removed and metallic alkyls were formed; by this means it was shown that aliphatic free radicals were intermediates in a large number of pyrolyses and photolyses. Two other methods were developed to accomplish this end. Hinshelwood showed in 1936 that the addition of very small quantities of nitric oxide to the reacting system greatly inhibited the pyrolysis of many organic vapours. Nitric oxide is a molecule containing an odd number of electrons and it was expected that it would combine very rapidly with free radicals

to give a compound with the usual even number of electrons. Since the free-radical chain-carriers in a pyrolysis are present in very small concentrations (often of the order of 10^{-10} mole per l.), a very small quantity of nitric oxide should greatly inhibit the overall reactions. Hinshelwood also showed that propene in larger quantities had a similar effect. Hence reactions which are inhibited by nitric oxide and propene probably involve free radicals. Patat and Sachsse showed that the reacting mixtures in pyrolyses would accelerate the ortho-para-hydrogen conversion, as would be expected if free radicals were involved. All of these techniques and their applications to particular systems are described fully in Steacie's definitive monograph.¹

The theory needed to explain many of these observations was provided by Rice and Herzfeld, who showed that the experimental data on pyrolysis reactions *could* be interpreted on the basis of free-radical mechanisms involving several simple elementary processes about which reasonable assumptions could be made. At that time no particular mechanism could be rigorously tested because not enough was known about the elementary reactions. Even today our knowledge of some of the postulated steps is inadequate for unequivocal judgments of the mechanisms favoured by Rice. However, it has been shown that Rice's anticipation was often remarkably accurate. Steacie¹ gives very complete accounts of these mechanisms.

Modern Developments.—During the last decade the interest of most investigators has shifted from the qualitative study of complex systems to the quantitative study of the elementary processes occurring in pyrolyses, photolyses, and polymerisations. In order to avoid complicating side reactions, these reactions are normally carried to very low percentage conversions and in consequence the analytical problems are great. The researches have been made possible by advances in analytical technique and by the increasing availability of isotopic tracers. The important analytical techniques which were mostly developed for oil companies in the United States are low-temperature distillation, Blacet and Leighton's analysis system,² and the analytical mass-spectrometer; as yet, the recording infra-red spectrometer has been comparatively little used in the study of free-radical reactions. As examples of the power of these methods it may be mentioned that by low-temperature distillation it is now possible to estimate 0.1 ml. (S.T.P.) of ethane in the presence of 15 ml. of propane to an accuracy of $\pm 3\%$ in $1\frac{1}{2}$ hours. The proportion of ethylene in an ethylene-ethane sample of 20 μ l. may be determined in 40 minutes to an accuracy of $\pm 0.05 \mu$ l. with Blacet and Leighton's apparatus. Under favourable conditions the proportion of CD_3H in CD_4 may be determined in 15 minutes to better than 0.1% on a mass-spectrometer. These are powerful new tools for the investigation of gas-reactions.

The Types of Methyl-radical Reaction.—There are three principal classes of methyl-radical reaction :

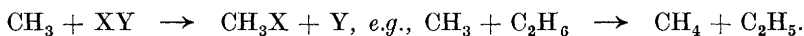
1. *Combination reactions* : $CH_3 + XY \rightarrow CH_3XY$, e.g., $CH_3 + CH_3 \rightarrow C_2H_6$. Methyl radicals will combine with methyl radicals, other free

¹ "Atomic and Free Radical Reactions", Reinhold, New York, 1947.

² *Ind. Eng. Chem. Anal.*, 1931, **3**, 266.

radicals, atoms, or "odd electron" molecules to give normal saturated molecules.

2. Metathetical reactions :



Methyl radicals will extract atoms from molecules to produce saturated methyl derivatives and a new free radical or atom. This class of methyl-radical reaction has been intensively studied, especially those reactions in which a hydrogen atom is extracted. At least two cases of the extraction of a radical from a molecule are known, namely, that of acetyl from diacetyl and that of methyl from dimethylmercury.

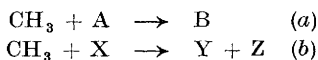
3. *Addition reactions*: $\text{CH}_3 + \text{XY} \rightarrow \text{CH}_3\text{XY}$, e.g., $\text{CH}_3 + \text{C}_2\text{H}_4 \rightarrow \text{C}_3\text{H}_7$. Methyl radicals will add to molecules containing multiple bonds to give more complex free radicals.

Only these three types of methyl-radical reaction have been established beyond reasonable doubt. All the more complex alkyl radicals can undergo the following two other sorts of reaction which make the study of their behaviour very difficult.

4. *Decomposition reactions*: e.g., $\text{C}_2\text{H}_5 \rightarrow \text{C}_2\text{H}_4 + \text{H}$. That decomposition reactions of this type occur has been established, but very few have been studied quantitatively because there are few suitable radical sources. Mercury photosensitisation has so far proved to be the best source, and the decomposition of the radicals derived from the abstraction of a hydrogen atom from ethane,³ propane,⁴ *n*-butane, 2-methylpropane,⁵ methyl alcohol,⁶ and dimethyl ether⁷ has been studied in this way. The reaction $\text{CH}_3 \rightarrow \text{CH}_2 + \text{H}$ is theoretically possible but probably has an activation energy of at least 80 kcal. and will not become appreciable until temperatures of 1000° K are reached. By contrast, the decomposition of the *n*-butyl radical can be detected at 500° K.

5. *Disproportionation reactions*: e.g., $\text{C}_2\text{H}_5 + \text{C}_2\text{H}_5 \rightarrow \text{C}_2\text{H}_6 + \text{C}_2\text{H}_4$. Very little is known about reactions of this type, but they certainly occur under some conditions, for Ivin and Steacie⁸ have accurately studied the disproportionation of ethyl radicals in the photolysis of diethylmercury. The only evidence for the reaction $\text{CH}_3 + \text{CH}_3 \rightarrow \text{CH}_4 + \text{CH}_2$ comes from the work of Bawn and Tipping⁹ which appears to be quite unrelated to normal work on homogeneous gas-phase reactions, probably because the reaction was studied in an atmosphere of sodium vapour.

From this list we can see that all known reactions of methyl radicals are bimolecular at high pressures. Consequently, the reactions may be



³ Bywater and Steacie, *J. Chem. Physics*, 1951, **19**, 172.

⁴ *Idem, ibid.*, p. 319.

⁵ *Idem, ibid.*, p. 326.

⁶ Phibbs and Darwent, *ibid.*, 1950, **18**, 495.

⁷ Marcus, Darwent, and Steacie, *ibid.*, 1948, **16**, 987.

⁸ *Proc. Roy. Soc.*, 1951, *A*, **208**, 25.

⁹ *Discuss. Faraday Soc.*, 1947, **2**, 104.

represented by equation (a) or (b). In these two cases the respective rate constants k_a and k_b are defined by the equations

$$R_b \equiv d[B]/dt = - d[A]/dt = k_a[\text{CH}_3][A]$$

and $R_y \equiv d[Y]/dt = R_z \equiv d[Z]/dt = - d[X]/dt = k_b[\text{CH}_3][X]$

where the letters in brackets are the concentrations of the substances and R_y is the rate of formation of Y, and so on : this notation will be used throughout. Hence if the methyl-radical concentration is known, the rate constant in the first case can be found by measuring the formation of B or the disappearance of A, and in the second case by the disappearance of X or the formation of Y or Z.

The rate constants all obey the Arrhenius equation $k = A \exp(-E/RT)$ within the limits of experimental error, where E is the activation energy of the reaction and A , which is usually called the pre-exponential or A factor, is a number having the dimensions of a rate constant. The Arrhenius equation may be written in terms of the collision theory of chemical kinetics for a bimolecular reaction as $k = PZ \exp(-E/RT)$, where P is known as the steric factor, and Z , the collision frequency of the reacting species, is given by

$$Z = \sigma_{x,y}^2 \left[8\pi kT \frac{(m_x + m_y)}{m_x m_y} \right]^{\frac{1}{2}}$$

where $\sigma_{x,y}$ is the mean molecular (collision) diameter of X and Y ; m_x and m_y are the masses of the respective molecules, and k is Boltzmann's constant.

The great value of the collision theory is that it provides a very simple picture of chemical kinetics, as a large number of reactions is known in which $P = 1$. A weakness is that Z is not a well-defined quantity, because of the uncertainty as to the appropriate values for the collision diameters. To preserve the simplicity of the theory, collision diameters which might be determined by viscosity and other methods depending on the transport properties of the gases should be selected. Almost all workers on methyl radicals have done this when calculating steric factors, but despite the uniformity of practice it is probably less likely to cause confusion if the directly determinable A factors are given. Throughout this Review, A factors will be quoted but for purposes of comparison and as an *aide-mémoire* the two following values of Z are given :

Z for the collision of two methyl radicals at 455°K with collision diameters of $3.5 \text{ \AA} = 2 \times 10^{-10} \text{ molecules}^{-1} \text{ c.c. sec.}^{-1} = 1 \times 10^{14} \text{ mole}^{-1} \text{ c.c. sec.}^{-1}$.

Z for the collision of a methyl radical at 455°K with a molecule of molecular weight 50 and a collision diameter of $5.5 \text{ \AA} = 6 \times 10^{-10} \text{ molecules}^{-1} \text{ c.c. sec.}^{-1} = 4 \times 10^{14} \text{ mole}^{-1} \text{ c.c. sec.}^{-1}$.

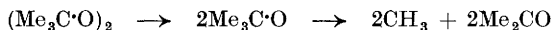
There are two principal difficulties which must now be considered in the study of methyl radicals : first, a suitable source of them must be selected, and secondly, some way of determining the steady state concentration of methyl radicals, usually about $10^{-12} \text{ mole/c.c.}$, must be found.

Sources of Methyl Radicals.—Hitherto the methyl radicals required for

kinetic studies have almost always been produced by either the pyrolysis or the photolysis of compounds containing methyl groups. For most purposes photolyses are more convenient because they are easily controlled and can be used over a wide range of temperature. Unfortunately, all convenient pyrolyses have activation energies at least three times that of the majority of methyl-radical reactions, so the accessible temperature range of study, and hence the accuracy of the determination of activation energy, is much reduced.

The most widely used photolytic sources are acetone, dimethylmercury, acetaldehyde, azomethane, and methyl iodide, of which acetone is far the best. Acetone is convenient because it is readily obtainable, is relatively unreactive and thermally stable, and has a convenient vapour pressure and a broad absorption band in the near ultra-violet, and a measure of the carbon monoxide produced can be used as an internal actinometer. Moreover, through the work of W. A. Noyes, junr., and his school¹⁰ its photolysis is very well understood.

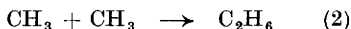
The best pyrolytic source of methyl is di-*tert.*-butyl peroxide, which decomposes in two stages:



its big disadvantage is that the decomposition has an activation energy of about 37 kcal.,^{11, 12} and so it can only be used in the temperature range 130–170° c. Acetyl peroxide¹³ in solution and azomethane¹⁴ in the vapour have also been used as pyrolytic radical sources.

Methods of Investigation.—The difficulty of determining methyl-radical concentrations cannot be dealt with apart from the general problems of this type of study which we will consider now.

Noyes and his school¹⁰ have shown that when acetone is photolysed above 100° c all the methane and ethane can be quantitatively accounted for by the reactions (2) and (3):*



Now

$$R_{\text{C}_2\text{H}_6} = k_2[\text{CH}_3]^2 \quad \text{and} \quad R_{\text{CH}_4} = k_3[\text{CH}_3][\text{CH}_3\cdot\text{CO}\cdot\text{CH}_3]$$

Hence

$$R_{\text{CH}_4}/R_{\text{C}_2\text{H}_6}^{\frac{1}{2}} = k_3[\text{CH}_3\cdot\text{CO}\cdot\text{CH}_3]/k_2^{\frac{1}{2}}$$

and

$$k_3/k_2^{\frac{1}{2}} = R_{\text{CH}_4}/R_{\text{C}_2\text{H}_6}^{\frac{1}{2}}[\text{CH}_3\cdot\text{CO}\cdot\text{CH}_3] = A_3e^{-E_3/RT}/A_2^{\frac{1}{2}}e^{-\frac{1}{2}E_2/RT}$$

Therefore by determining this ratio over a range of temperatures, $E_3 - \frac{1}{2}E_2$ and $A_3/A_2^{\frac{1}{2}}$ can be found.

Furthermore, in principle, when a photolytic system involves reactions

¹⁰ W. A. Noyes, junr., and Dorfman, *J. Chem. Physics*, 1948, **16**, 788.

¹¹ Raley, Rust, and Vaughan, *J. Amer. Chem. Soc.*, 1950, **70**, 88.

¹² Murawski, Roberts, and Szwarc, *J. Chem. Physics*, 1951, **19**, 698.

¹³ Edwards and Mayo, *J. Amer. Chem. Soc.*, 1950, **72**, 1265.

¹⁴ A. O. Allen and Sickman, *ibid.*, 1934, **56**, 2031.

* For reaction (1), see p. 203.

of the type $M + h\nu = nA$, $A + B = X$, and $2A = Y$, so that the rate of formation of one product is dependent upon the first power of the concentration of A and the rate of formation of the second is dependent upon the second power of this concentration, it is possible to use the method of intermittent illumination to find the two rate constants involved. In two recent articles¹⁵ reference has been made to the application of the method of intermittent illumination to the determination of absolute rate constants in polymerisation and liquid-phase oxidation reactions. A full description of the mathematical theory of the method has been given by Burnett and Melville.¹⁶ A "pilot" reaction of the type $A + B = X$ is used to measure the average concentration of the transient radical A during the run, for if B is in excess the average concentration of A is directly proportional to the rate of production of X. However, while sufficient quantities of X must be obtained for accurate analysis it is essential that the concentration of A in the system should not be appreciably disturbed owing to formation of X. In the polymerisations and oxidations this difficulty does not arise because the over-all chain process may be used as the "pilot" reaction, in which a new radical is formed each time the radical A reacts with B; but for the study of methyl-radical reactions, high light intensities and low temperatures must be used, so the amount of methyl reacting with B is a negligible (*ca.* 0.5%) part of the total amount of methyl released in the system. All the accurate absolute rate constants of methyl-radical reactions are based upon rotating sector determinations of the rate of methyl-radical combination.

When a mixture of acetone and another hydrogen-containing compound



is photolysed the reaction (1) will take place as well as reactions (2) and (3). Now

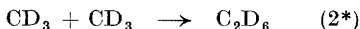
$$R_{\text{CH}_4} = k_3[\text{CH}_3][\text{CH}_3 \cdot \text{CO} \cdot \text{CH}_3] + k_1[\text{CH}_3][\text{RH}]$$

and

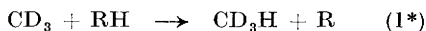
$$R_{\text{CH}_4}/R_{\text{C}_2\text{H}_6}^{\frac{1}{2}} = k_3[\text{CH}_3 \cdot \text{CO} \cdot \text{CH}_3]/k_2^{\frac{1}{2}} + k_1[\text{RH}]/k_2^{\frac{1}{2}}$$

But the term $k_3[\text{CH}_3 \cdot \text{CO} \cdot \text{CH}_3]/k_2^{\frac{1}{2}}$ has already been determined, so $k_1/k_2^{\frac{1}{2}}$ and consequently $E_1 - \frac{1}{2}E_2$ and $A_1/A_2^{\frac{1}{2}}$ can be found. All the results listed in Tables 3 and 4, for which the radical source was acetone or dimethyl-mercury, were obtained in this way.

An alternative procedure is to use fully-deuterated acetone, for which $k_3^*/k_2^{*\frac{1}{2}}$ may be obtained as before for reactions (3*) and (2*):



In the presence of a hydrogen-containing compound, reaction (1*) occurs:



Hence

$$k_1^*/k_3^* = R_{\text{CD}_3\text{H}}[\text{CD}_3 \cdot \text{CO} \cdot \text{CH}_3]/R_{\text{CD}_4}[\text{RH}]$$

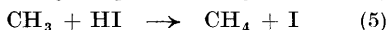
The ratio $R_{\text{CD}_3\text{H}}/R_{\text{CD}_4}$ can be rapidly and accurately determined, so k_1^*/k_3^*

¹⁵ Bolland, *Quart. Reviews*, 1949, **3**, 1; Burnett, *ibid.*, 1950, **4**, 292.

¹⁶ *Proc. Roy. Soc.*, 1947, *A*, **189**, 456.

can be found. Since the relation between k_3^* and k_3 has been determined, this is a method of finding k_1 . All the results listed in Tables 3 and 4, for which the radical source was hexadeuteroacetone, were obtained in this way.

An extension of this principle is involved in the method which has been used for the study of very fast methyl reactions. If the number of methyl radicals produced in a system is known, and there are only two methods by which the radicals can disappear, such as reactions (4) and (5)



then

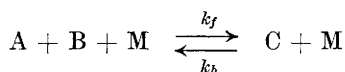
$$R_{\text{CH}_4} = k_5[\text{CH}_3][\text{HI}]$$

$$R_{\text{CH}_3\text{I}} = \text{Rate of methyl production} - R_{\text{CH}_4} = k_4[\text{CH}_3][\text{I}_2]$$

$$\text{Therefore } k_5/k_4 = \frac{R_{\text{CH}_4}[\text{I}_2]}{[\text{Rate of methyl production} - R_{\text{CH}_4}][\text{HI}]}$$

Unfortunately, k_4 has not yet been determined absolutely, so only relative constants are obtained by this method.

The Combination Reactions of Methyl Radicals.—Because the methyl radical contains only four atoms, one of them heavy and three light, there is a possibility that the rate of methyl-radical combination with other small radicals and atoms will be markedly dependent on the pressure in the system in which the reaction is studied owing to third-body effects. This phenomenon is the exact converse of that observed in those unimolecular decomposition reactions the rate of which falls off at low pressures, and is similar to the third-body effect observed in the combination of hydrogen, bromine, and iodine atoms. Lindemann, O. K. Rice, Ramsperger, and Kassel¹⁸ have developed the basic quantitative treatment of these "quasi-unimolecular" reactions. It is usually convenient when dealing with combination reactions to make use of the relation $k_f/k_b = K$, where the rate and equilibrium constants refer to the reactions



The problem of the combination of A + B in the presence of a third body can then be "inverted" so as to be the problem of the decomposition of C in the presence of a neutral gas. Thus stated, the problem is more tractable for a number of reasons including the fact that the definition of a two-body collision is clear-cut whereas that of a three-body collision is not. Marcus and Rice¹⁹ recently considered the effect of pressure in the combination of methyl radicals with other methyl radicals and with iodine atoms. They concluded that energy-transfer effects should become important in the region of a few millimetres' pressure for the combination of methyl radicals

¹⁷ *J. Chem. Physics*, 1951, **19**, 85.

¹⁸ See L. S. Kassel, "Kinetics of Homogeneous Gas Reactions", Chemical Catalog Co., New York, 1932.

¹⁹ *J. Phys. Colloid Chem.*, 1951, **55**, 894; see also Marcus, *J. Chem. Physics*, 1952, **20**, 359.

and at pressures of hundreds of millimetres for the combination of methyl with an iodine atom.

The most important combination reaction of methyl radicals is that in which two of them combine to give ethane. This reaction has been very accurately studied by Gomer and Kistiakowsky,¹⁷ who used the photolysis of both acetone and dimethylmercury as radical sources, the total pressure in the reaction system being 10–50 mm. Using the rotating sector technique, they found the rate constants given in Table 1, where k_2 is in mole⁻¹ c.c. sec.⁻¹. From these figures it may be seen that the activation

TABLE 1. *Rate constants for the combination of methyl radicals*

Radical source	Temp.	$k_2 \times 10^{-13}$	Radical source	Temp.	$k_2 \times 10^{-13}$
Acetone	125°	4.5	Dimethylmercury .	175°	4.6
Acetone	175	4.2	Dimethylmercury .	220	6.7

energy of the reaction is very low and that the collision yield for the reaction is about 0.5. This work seems to be very reliable, and the results obtained will be used throughout this Review for the calculation of rate constants based on the rate of formation of ethane in systems at relatively high pressures. In fact, most methyl-radical reactions have been investigated in systems at pressures of 50–100 mm. where the rate constant for the combination reaction is almost independent of pressure. The first attempts to detect the falling-off of the rate constant for methyl combination were not conclusive,²⁰ largely because experimental errors and complications increased markedly as the pressure was lowered so that it was difficult to be sure that the observed trend was not fortuitous. However, Kistiakowsky and Kirk Roberts²¹ have now found that the rate constant for the combination of methyl radicals definitely falls to about one-third of its high-pressure value when the total pressure in the system is reduced to 1 mm. This is in good agreement with Marcus's prediction.¹⁹

Lossing, Tickner, and Ingold have also measured the rate of combination of methyl radicals by a mass-spectrometric method²² by which it is possible to observe directly the concentration of methyl radicals and ethane in a flow-reaction vessel attached to the ionisation chamber of the mass-spectrometer. Di-*tert.*-butyl peroxide, dimethylmercury, and ethylene oxide at a few microns' pressure in the presence of 5–19 mm. of helium as a carrier gas have been used as radical sources. The rate constant found at 160° c agrees within 50% with those of Gomer and Kistiakowsky at high pressures. The rate constant decreases with increasing temperature according to the equation $k \propto \exp[(2200 \pm 500)/RT]$ over the range from 160° to 800° c.

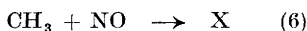
²⁰ Trotman-Dickenson and Steacie, *J. Chem. Physics*, 1950, **19**, 1097; Nicholson, *J. Amer. Chem. Soc.*, 1951, **73**, 3981; Linnell and W. A. Noyes, junr., *ibid.*, p. 3986.

²¹ Personal communication.

²² Lossing and Tickner, *J. Chem. Physics*, 1952, **20**, 907; Lossing, K. U. Ingold, and Tickner, *Discuss. Faraday Soc.*, 1953, **14**; also personal communication from Dr. Lossing.

Surprisingly; no evidence was found for the variation of rate with helium pressure.

The only other combination reaction which has been quantitatively studied is that of methyl with nitric oxide. The products of the reaction (6) are not known with certainty and are complex. Formaldoxime, ammonia,



hydrogen cyanide, and carbon monoxide have all been detected, so it is likely that a single molecule, perhaps CH_3NO , is first formed, which is unstable under the conditions of the experiment and rearranges or decomposes to give the observed products. The reaction has been studied by two methods, the first for the pressure range 5–100 mm. and the second for the range around 0.2 mm. Since the complex formed as a result of the reaction contains only six atoms, it would not be surprising if this rate constant were also dependent upon pressure, and this appears to be the case.

In the first method²³ the reaction is studied by photolysing acetone or dimethylmercury in the presence of nitric oxide at room temperature. A very low concentration of nitric oxide is kept constant by steadily leaking a known quantity of the gas into the reaction vessel during the run. After a convenient time (t) the reaction mixture was analysed for ethane and nitric oxide. Now

$$[\text{C}_2\text{H}_6] = tk_2[\text{CH}_3]^2$$

$$\text{and total NO consumed} = tk_6[\text{CH}_3][\text{NO}]$$

The amount of nitric oxide found on analysis may be regarded as the steady-state concentration, for some 200 times this amount is added during the course of the run. From these equations and the accepted value of k_2 , k_6 is found to be 2×10^{11} mole⁻¹ c.c. sec.⁻¹ at 28° C over the whole range of pressure.

The second method, first used by Forsyth,²⁴ has been greatly improved by Durham and Steacie,²⁵ who produced the methyl radicals by passing a stream of di-*tert.*-butyl peroxide through a furnace and down a tube into which nitric oxide could be injected. The concentration of methyl radicals at any point in the tube could be measured by following the rate of removal of a radioactive tellurium mirror. In this way the effect of the pressure of nitric oxide on the radical concentration along the reaction tube could be found, and hence the rate constant for the reaction of the radicals with nitric oxide. The value of $k_6 = 3.3 \times 10^{10}$ mole⁻¹ c.c. sec.⁻¹ at 25° C is much lower than the high-pressure value, but as there is no reason to suspect the experimental accuracy of either determination, this difference must be ascribed to the pressure dependence of the rate constant. Unfortunately, insufficient is known about the products of reaction (6) for the phenomenon to be treated theoretically.

A mass-spectrometer can also be used for methyl-radical detection,²²

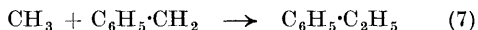
²³ Marcus and Steacie, *Z. Naturforsch.*, 1949, **4**, a, 332; Miller and Steacie, *J. Chem. Physics*, 1951, **19**, 73.

²⁴ Forsyth, *Trans. Faraday Soc.*, 1941, **37**, 312.

²⁵ *J. Chem. Physics*, 1952, **20**, 582.

and in this way the rate constant was found to be 10^{11} mole⁻¹ c.c. sec.⁻¹ at 950° c, with rather a large experimental error ; however, this figure may be taken as good evidence that the activation energy of the reaction is very small indeed.

It is generally believed that a large number of combinations of methyl radicals with other radicals occur, but only in a few cases have the products been identified, because of the analytical difficulties involved in the separation of small quantities of R·CH₃ from large quantities of RH, where R is a large radical. However, the products of the combination of methyl with acetyl, acetyl, *n*-propyl, and *isopropyl* have all been found, though none of the rate constants has been measured. Ivin and Steacie⁸ have found that ethyl radicals combine on about one collision in two to give butane, so it is very probable that the reactions of methyl with ethyl and of methyl with propyl have similar collision yields. These combinations of methyl with large radicals may be regarded as independent of pressure under all accessible conditions. The combination of methyl with a benzyl radical, reaction (7), has not been detected but there is no reason to suppose that it



does not occur. The activation energy for the decomposition of ethylbenzene as measured by Szwarc²⁶ may be combined with the C-H bond strengths in toluene and methane and the heats of formation of toluene, methane, and ethylbenzene to give the activation energy of reaction (7) as 1 ± 4 kcal. Furthermore, if reasonable assumptions are made about the properties of the methyl and benzyl radicals, the entropy change in the reaction may be calculated and hence the equilibrium between methyl and benzyl radicals and ethylbenzene. On this basis the rate constant of reaction (7) at 182° c has been found to be 10^{12} mole⁻¹ c.c. sec.⁻¹, E_7 being assumed equal to 0 kcal. This result is probably not very accurate.

It may be supposed that under suitable conditions methyl radicals would combine with atoms, but there is little direct evidence for such reactions. The rate constants will certainly be very dependent upon the total pressure of gas in the system, and it is likely that the "high-pressure" rate will only be approached at several atmospheres, which is not a usual pressure at which to study free radicals. Under the normal conditions of flow pyrolysis, the rates of the reverse reactions, the decompositions of methyl bromide²⁷ and methyl iodide,²⁸ are markedly dependent upon the overall pressure.

The quantitative data on the combination of methyl radicals are summarised in Table 2, where k and A are in mole⁻¹ c.c. sec.⁻¹. There is very little quantitative information on the rates of combination of other small radicals, though in a fair number of cases the products have been detected. The satisfactory interpretation of a very large amount of information on pyrolysis reactions such as have been described by Szwarc²⁹ has been based

²⁶ *J. Chem. Physics*, 1949, **17**, 431.

²⁷ Schon and Szwarc, *Proc. Roy. Soc.*, 1951, *A*, **209**, 110.

²⁸ Horrex and Lapage, *Discuss. Faraday Soc.*, 1951, **10**, 233.

²⁹ *Chem. Reviews*, 1950, **47**, 75.

upon the supposition that small radicals always combine with zero activation energy. On these grounds, rather than as a result of direct experiments, we must conclude that simple radicals combine with very low activation energies. At the other end of the scale of molecular size it is known¹⁵ that growing polymer radicals combine with low activation energies but that the rate constants are usually lower than for small radicals, being of the order of 10^{10} mole⁻¹ c.c. sec.⁻¹.

TABLE 2. *Combination reactions of methyl radicals*

Reaction	k at 182° c	A	E , kcal.
$\text{CH}_3 + \text{CH}_3 \rightarrow \text{C}_2\text{H}_6$ $\text{CH}_3 + \text{C}_6\text{H}_5\cdot\text{CH}_2 \rightarrow \text{C}_6\text{H}_5\cdot\text{C}_2\text{H}_5$	4.5×10^{13} (10^{12})	4.5×10^{13} (10^{12})	0 ± 0.7 1 ± 4
$\text{CH}_3 + \text{NO} \rightarrow \text{X}$	2×10^{11} (at 28° c)	2×10^{11} (min.)	4.5 (max.)

Metathetical Reactions of Methyl Radicals.—As yet only the class of metathetical methyl radical reactions represented by the general equation $\text{CH}_3 + \text{RH} \rightarrow \text{CH}_4 + \text{R}$ has been comprehensively studied in a quantitative manner. There are two good reasons for this, the first being that the important products of these reactions from the point of view of a kinetic study, *viz.*, methane and ethane, are fairly easily separated from the rest of the reaction mixture by distillation. Other difficulties apart, an investigation of, for example, the reaction $\text{CH}_3 + \text{C}_5\text{F}_{12} \rightarrow \text{CH}_3\text{F} + \text{C}_5\text{F}_{11}$ would be complicated because CH_3F and C_2H_6 have boiling points which are very close together, so a mass-spectrometer is needed for analysis. The second reason is that our knowledge of the dissociation energies of C-H bonds is more extensive²⁹ than of those between any other two atoms. It has long been thought that there should be a relation between the strength of a bond and the ease with which the atom attached by the bond can be removed by free-radical attack. Much research has been carried out with this possibility in mind.

The first extensive work on reactions of the type mentioned was that of H. S. Taylor with Cunningham³⁰ and with Smith.³¹ They investigated the photolysis of dimethylmercury in the presence of hydrogen, deuterium, ethane, *n*-butane, 2-methylpropane, and *neopentane* and several unsaturated and aromatic compounds. It has been shown³² that in the majority of cases not very much reliance can be placed upon the quantitative aspects of the work, but the general pattern of the results which they obtained was undoubtedly correct. They found that the activation energy for the reaction of methyl with an alkane containing only primary hydrogen atoms was greater than that for reaction with one containing secondary hydrogen atoms which in turn was greater than that for one containing a tertiary

³⁰ *J. Chem. Physics*, 1938, **6**, 359.

³¹ *Ibid.*, 1939, **7**, 390; 1940, **8**, 543.

³² Steacie, Darwent, and Trost, *Discuss. Faraday Soc.*, 1947, **2**, 79; Trotman-Dickenson and Steacie, *J. Phys. Colloid Chem.*, 1951, **55**, 908.

hydrogen. In addition it was found that the reaction with toluene and propene was rapid, while that with benzene was slow. All these points have been verified by later investigations.

Shortly afterwards, Allen³³ used the photolysis of acetone to investigate the reactions of methyl with propane. The investigation was cursory and the results obtained are not of quantitative significance.

In the last few years a large number of methyl-radical reactions of this type have been investigated, chiefly at the University of Rochester, N.Y., and in the laboratories of the National Research Council of Canada in Ottawa. The results were obtained by the methods outlined above. All of the results which are suitable for tabular presentation are included in Tables 3 and 4. Before considering their significance, we will try to assess their accuracy.

TABLE 3. *Reactions of methyl radicals with hydrogen*

Radical source	Hydrogen isotope	E , kcal.	k (at 182° c) $\times 10^{-6}$	$A \times 10^{-10}$	Ref
HgMe ₂	H ₂	9.3 ± 0.5	14	30	34
Acetone	H ₂	9.2 ± 0.3	5	15	35
CdMe ₂	H ₂	13 ± 2	14	2500	36
Acetone	H ₂	13.2 ± 0.4	1.5	300	37
Acetaldehyde . .	H ₂	15.3 ± 1.0	25	60,000	37
Acetone	D ₂	11.7 ± 0.2	1.5	70	35
Acetone	D ₂	14.3 ± 0.6	0.5	300	37
Acetone- <i>d</i> ₆ . . .	H ₂	10.2 ± 0.2	6	50	35
Acetone- <i>d</i> ₆ . . .	D ₂	10.9 ± 0.3	2	40	35

The most remarkable feature of the figures is the excellence of the agreement obtained by different workers using different sources of methyl radicals and usually different types of radiation when the same substance is photolysed. This gives us great confidence that the results are accurate and that no complications due to "hot" radicals arise. The rate constant k at 182° c is the most directly determinable quantity; this temperature is chosen as being near the middle of the temperature range of most investigations. Different workers usually agree on the magnitude of this rate within a factor of 1.5. In a series of experiments values can usually be reproduced to within $\pm 10\%$. The probable errors in the activation energies are given in the table; these errors are derived solely from the deviations of the points from the Arrhenius relationship; no weight is given to uncertainties in the assumed mechanism. The values for the activation energy are based on $E_2 = 0$ kcal., and the values of A_1 on $A_2 = 4.5 \times 10^{13}$ moles⁻¹ c.c. sec.⁻¹. It should be noted that errors in the differences of

³³ *J. Amer. Chem. Soc.*, 1941, **63**, 708.

³⁴ Phibbs and Darwent, *Trans. Faraday Soc.*, 1949, **45**, 541.

³⁵ Majury and Steacie, *Discuss. Faraday Soc.*, 1953, **14**.

³⁶ Anderson and H. A. Taylor, *J. Phys. Chem.*, 1952, **56**, 498.

³⁷ Davison and Burton, *J. Amer. Chem. Soc.*, 1952, **74**, 2307.

TABLE 4. *Metathetical reactions of methyl radicals* *

Reactant	Radical source †	<i>E</i> , kcal.	<i>k</i> × 10 ⁻⁶	<i>A</i> × 10 ⁻¹⁰	Ref.‡
Alkanes					
Methane	Acetone- <i>d</i> ₆	12.8	0.17	(Assumed)	38
Ethane	Acetone- <i>d</i> ₆	10.4 ± 0.4	2.0	19	39
<i>neo</i> Pentane	Acetone and acetone- <i>d</i> ₆	10.0 ± 0.3	3.3	20	39
2 : 2' : 3 : 3-Tetramethylbutane	Acetone- <i>d</i> ₆	9.5 ± 0.4	5.2	17	39
<i>n</i> -Butane	Acetone	8.3 ± 0.2	11	11	39
	HgMe ₂	8.2 ± 0.5	22	18	40
	HgMe ₂	9.5 ± 0.5	10	33	40 [‡]
	HgMe ₂	—	13	—	31 [‡]
<i>n</i> -Pentane	Acetone	8.1 ± 0.2	14	10	39
<i>n</i> -Hexane	Acetone	8.1 ± 0.2	17	12	39
2-Methylpropane	Acetone	7.6 ± 0.2	22	10	39
	HgMe ₂	7.3 ± 0.3	16	6	41
	Azomethane	6.6 ± 0.3	10	2	42
2 : 3-Dimethylbutane	Acetone	6.9 ± 0.2	35	7	39
	Acetone- <i>d</i> ₆	7.8 ± 0.4	40	21	39
2 : 3 : 4-Trimethylpentane	Acetone- <i>d</i> ₆	7.9 ± 0.4	34	20	39
Alkenes					
Ethene	Acetone- <i>d</i> ₆	10.0 ± 0.4	2.9	17	43
Propene	Acetone- <i>d</i> ₆	7.7 ± 0.4	12	6	43
But-2-ene	Acetone- <i>d</i> ₆	7.7 ± 0.4	30	14	43
2-Methylprop-2-ene	Acetone- <i>d</i> ₆	7.3 ± 0.4	26	8	43
2 : 3-Dimethylbut-2-ene	Acetone- <i>d</i> ₆	7.8 ± 0.4	76	40	43
But-1-ene	Acetone- <i>d</i> ₆	7.6 ± 0.4	34	15	43
Pent-1-ene	Acetone- <i>d</i> ₆	7.6 ± 0.4	35	15	43
3-Methylbut-1-ene	Acetone- <i>d</i> ₆	7.4 ± 0.4	53	18	43
Alkynes					
But-2-yne	Acetone- <i>d</i> ₆	8.6 ± 0.4	33	42	44
But-1-yne	Acetone- <i>d</i> ₆	9.1 ± 0.4	34	76	44
Cyclanes					
<i>cyclo</i> Propane	Acetone- <i>d</i> ₆	10.3 ± 0.4	1.1	9	44
	HgMe ₂	10.2 ± 1.0	1.5	12	45
<i>cyclo</i> Butane	Acetone- <i>d</i> ₆	9.3 ± 0.4	11	28	44
<i>cyclo</i> Pentane	Acetone and acetone- <i>d</i> ₆	8.3 ± 0.2	24	24	44
<i>cyclo</i> Hexane	Acetone	8.3 ± 0.2	22	22	44
Aromatic hydrocarbons					
Benzene	Acetone- <i>d</i> ₆	9.2 ± 0.4	1.0	2.5	44
Toluene	Acetone- <i>d</i> ₆	8.3 ± 0.3	14	14	44
	HgMe ₂	7 ± 2	5	1	31 [‡]
	DTBP	11 ± 2	—	—	46
Alcohols					
Methanol	Acetone	8.2 ± 0.2	6	4.8	44
	HgMe ₂	8.2 ± 0.5	5	4.4	45
Ethanol	Acetone- <i>d</i> ₆	8.7 ± 0.4	20	29	44
Propan-2-ol	Acetone- <i>d</i> ₆	7.3 ± 0.4	31	10	44

* Values of *k* refer to 182° c, and both *k* and *A* are expressed in terms of moles⁻¹ c.c. sec.⁻¹.

† DTBP = Di-*tert*-butyl peroxide.

‡ Where this mark is appended to the reference it indicates that the quantities were not calculated in this manner by the original authors.

TABLE 4. *Metathetical reactions of methyl radicals* * (continued)

Reactant	Radical source †	<i>E</i> , kcal.	<i>k</i> × 10 ⁻⁶	<i>A</i> × 10 ⁻¹⁰	Ref. ‡
Amines and imines etc.					
Methylamine	Acetone- <i>d</i> ₆	8.4 ± 0.4	19	20	44
Dimethylamine	Acetone- <i>d</i> ₆	7.2 ± 0.4	70	19	44
Ethyleneimine	DTBP	4.8 ± 0.3	200	5	47
Trimethylamine	Acetone- <i>d</i> ₆	8.8 ± 0.4	44	70	44
Ammonia	Acetone- <i>d</i> ₆	10.0 ± 0.4	1.2	7	44
Azomethane	Azomethane	7.6	~ 20	~ 10	42
Ethers and epoxides					
Dimethyl ether	Acetone	9.5 ± 0.2	9	30	44
	HgMe ₂	8.4 ± 1.5	9	10	45
	CH ₂ ·O·CH ₃	10 ± 2	12	70	7 [‡]
Diisopropyl ether	Acetone- <i>d</i> ₆	7.3 ± 0.4	38	12	44
Ethylene oxide	HgMe ₂	9.0 ± 1.0	1.5	3	48
	HgMe ₂	9.6 ± 2	2.8	11	45
Aldehydes					
Acetaldehyde	DTBP	8.0 ± 0.3	220	90	49
Ketones					
Acetone	Acetone	9.7 ± 0.1	10	40	50
	Acetone	9.6 ± 0.4	8	30	51 [‡]
	Acetone	9.5 ± 0.2	11	40	17
	DTBP	9.5 ± 1.0	9	27	52
Acetone- <i>d</i> ₆	Acetone- <i>d</i> ₆	10.3 ± 0.2	4	40	50
	Acetone- <i>d</i> ₆	10.6 ± 0.3	6	70	35
Diacetyl	Diacetyl	7.1 ± 0.2	17	5	53
Peroxides					
Di- <i>tert.</i> -butyl peroxide . .	DTBP	(15)	2	(3000)	47 [‡]
Metal alkyls					
Dimethylmercury	HgMe ₂	9.0 ± 0.5	10	20	54
	HgMe ₂	11.0	3	40	41
Dimethylcadmium	CdMe ₂	(14)	2	(700)	36
Halogenated methanes					
Methyl fluoride	Acetone	8.7 ± 0.3	25	40	55
Methylene fluoride	Acetone	6.2 ± 0.3	30	3	55
Methyl chloride	Acetone	9.4 ± 0.3	25	70	55
Methylene chloride	Acetone	7.2 ± 0.3	60	20	55
Chloroform	Acetone	5.8 ± 0.3	100	6	55
	Acetone	6.8			56
Methyl bromide	Acetone	10.1 ± 0.3	40	300	55
Methylene bromide	Acetone	8.7 ± 0.3	100	150	55
Hydrogen halide					
Hydrogen chloride	Acetone	2.1	2 × 10 ⁵	200	56

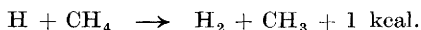
* Values of *k* refer to 182° c, and both *k* and *A* are expressed in terms of moles⁻¹ c.c. sec.⁻¹.

† DTBP = Di-*tert.*-butyl peroxide.

‡ Where this mark is appended to the reference it indicates that the quantities were not calculated in this manner by the original authors.

activation energies derived from a series of experiments on different compounds may often be much less than the errors in the *absolute* values. When this consideration is of importance for the interpretation of the experimental data attention will be drawn to the matter.

The results given in Table 3 for the reaction of methyl with hydrogen are taken straight from the original papers and show the confused state of the literature. The random experimental errors are quite likely to be on the low side but the discrepancies are too large to be assigned to this cause alone. Wijnen and Steacie⁵⁷ have shown that if, of those runs done by Davison and Burton,³⁷ one takes notice only of those in which the percentage conversion of the reactants was low and the photolysis was not likely to be complicated by side reactions, then the work gives a value of 10.5 ± 1 kcal./mole for the activation energy of the reaction. In their opinion all the most reliable published work leads to a value of 10.0 ± 0.5 kcal./mole for the activation energy. Unfortunately, this solution does not resolve all the difficulties, for the activation energy of the reaction



appears to be at least 12 kcal./mole, and therefore the back reaction must have an activation energy of at least 13 kcal./mole. No satisfactory explanation of this discrepancy has yet been given.

Several series of compounds have been studied sufficiently fully for it to be possible to draw certain conclusions about the trends in reactivity within the groups. The best investigated of all these series is that of the alkanes. Here it is apparent that the compounds fall into three groups of activation energies for the reaction with methyl of (i) about 10; (ii) about

³⁸ Trotman-Dickenson and Steacie, *J. Phys. Colloid Chem.*, 1951, **55**, 908.

³⁹ Trotman-Dickenson, Birchard, and Steacie, *J. Chem. Physics*, 1951, **19**, 163.

⁴⁰ Gomer, *J. Amer. Chem. Soc.*, 1950, **72**, 201.

⁴¹ Rebbert and Steacie, personal communication.

⁴² Jones and Steacie, personal communication.

⁴³ Trotman-Dickenson and Steacie, *J. Chem. Physics*, 1951, **19**, 169.

⁴⁴ *Idem*, *ibid.*, p. 329.

⁴⁵ Phibbs and Darwent, *Canadian J. Res.*, 1950, *B*, **28**, 395.

⁴⁶ Roberts and Szwarc, *Trans. Faraday Soc.*, 1950, **46**, 625.

⁴⁷ Brinton and Volman, *J. Chem. Physics*, 1952, **20**, 25.

⁴⁸ Gomer and W. A. Noyes, junr., *J. Amer. Chem. Soc.*, 1949, **71**, 3390.

⁴⁹ Brinton and Volman, *J. Chem. Physics*, 1952, **20**, 1053; there is strong evidence that this is the most reliable value, but for a different view see Dodd, *Trans. Faraday Soc.*, 1951, **47**, 56.

⁵⁰ Trotman-Dickenson and Steacie, *J. Chem. Physics*, 1950, **18**, 1097.

⁵¹ Saunders and H. A. Taylor, *ibid.*, 1941, **9**, 616.

⁵² Jacquiss, Roberts, and Szwarc, *J. Amer. Chem. Soc.*, 1952, **74**, 6005.

⁵³ Blacet and Bell, *Discuss. Faraday Soc.*, 1953, **14**.

⁵⁴ Gomer and W. A. Noyes, junr., *J. Amer. Chem. Soc.*, 1949, **71**, 3390.

⁵⁵ Raal and Steacie, *J. Chem. Physics*, 1952, **20**, 578. The error in these results is in some cases probably greater than is indicated because complicating side reactions may have occurred.

⁵⁶ Cvetanoviè and Steacie, *Canad. J. Chem.*, 1953, **31**, 158.

⁵⁷ *Discuss. Faraday Soc.*, 1953, **14**.

8.2, and (iii) less than 8 kcal./mole, and that these contain, respectively, (i) only primary, (ii) primary and secondary, (iii) primary and tertiary hydrogen atoms. Furthermore, since the A factors do not vary widely, this trend in activation energies is reflected by the trend in the rate constants. Now 2 : 2 : 3 : 3-tetramethylbutane contains three times as many primary hydrogen atoms as ethane, and 2 : 2-dimethylpropane twice as many. Since the three compounds all react with methyl with nearly the same activation energy, the hydrogen atoms in these compounds may be considered equivalent. Similarly, 2 : 3 : 4-trimethylpentane has three reactive tertiary hydrogen atoms, while 2 : 3-dimethylbutane has two and 2-methylpropane has one. We can by inspection decide how many "active" hydrogen atoms there are in an alkane and, after making a very small correction for the presence of less active types of hydrogen atoms in the compound, find by division the reaction rate characteristic of the "active" hydrogen atom. Thus for *n*-butane there are four "active" hydrogen atoms and six less active primary atoms. By consideration of the results obtained with compounds containing only primary hydrogen atoms, it can be found that the rate constant characteristic of a primary hydrogen atom at 182° C is *ca.* 3×10^6 mole⁻¹ c.c. sec.⁻¹. Hence for *n*-butane the rate constant characteristic of a secondary hydrogen atom is $\frac{1}{4}[11 - (6 \times 0.3)] = 2.3 \times 10^6$ mole⁻¹ c.c. sec.⁻¹. In this manner Table 5 has been obtained.

TABLE 5. *Rate constants characteristic of various types of hydrogen atoms in alkanes*

Type of hydrogen atom	10 ⁻⁶ <i>k</i> , characteristic, at 182° C (mole ⁻¹ c.c. sec. ⁻¹ /atom)
Primary	0.3, 0.2, 0.3
Secondary	2.3, 2.0, 2.0
Tertiary	18, 17, 10

This procedure is justified solely by the interesting nature of the results, which show that it is reasonable to regard the different types of hydrogen atom in a molecule as if they were present in separate molecules in a multi-component mixture.

In two recent reviews⁵⁸ reference has been made to a relation suggested by Polanyi between the heat of one reaction in a series and its energy of activation. Polanyi stated that, where there is no resonance stabilisation in the transition complex or a constant amount of stabilisation throughout a series, then for reactions of the type $X + YZ \rightarrow XY + Z$ it may be expected that $E = \alpha H + \text{const.}$, where E is the activation energy and H the heat of the reaction, and α has a value between 0 and 1. The results quoted above indicate that all primary C-H bonds and all secondary C-H bonds are very similar; if this uniformity is accepted, where the evidence is less

⁵⁸ Warhurst, *Quart. Reviews*, 1951, **5**, 44; Bolland, *ibid.*, 1950, **4**, 292.

good, for all tertiary C-H bonds we may generalise Stevenson's electron-impact data⁵⁹ as follows:

$D(\text{CH}_3\text{-H})$	102 kcal.	$D(\text{C-H})$, secondary	94 kcal.
$D(\text{C-H})$, primary	97 kcal.	$D(\text{C-H})$, tertiary	90 kcal.

From these figures, heats of reaction can be obtained for the reaction of methyl with each type of hydrogen atom; these values for the heats are plotted against the activation energies in Fig. 1. The value of E for $\text{CH}_3 + \text{CH}_4 \rightarrow \text{CH}_4 + \text{CH}_3$ was not determined directly, as the rate has effectively only been measured at one temperature. The straight line drawn in Fig. 1 is for $\alpha = 0.5$, which would be expected from considerations of symmetry based upon the similarity of the bonds broken and formed;

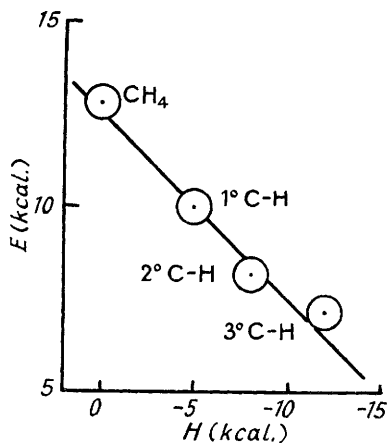


FIG. 1

The relation between activation energy and heat of reaction for the reactions of methyl radicals with alkanes:

$$E = 12.5 + 0.5H.$$

the positive deviation of the value of E for the tertiary hydrogen atom from the line might also be expected. This is the only case in which Polanyi's relation has been subjected to direct experimental test.

The striking fact about the results obtained from the study of the alkenes is that, apart from ethene, they all react with methyl with the same activation energy within the rather small limits of experimental error (the relative values of the activation energies are here good to 0.2 kcal./mole). It may be seen that, where possible, it is always the α -methylene hydrogen atom which reacts. Thus there are three "active" hydrogen atoms in propene, twelve in 2:3-dimethylbut-2-ene, two in but-1-ene and one in 3-methylbut-1-ene. In Table 6 are given the rate constants per active hydrogen atom for primary, secondary, and tertiary α -methylene hydrogen atoms and, assuming a constant value of E of 7.6 kcal., the values of A divided by the number of active hydrogen atoms. This table shows, first, that each type of hydrogen atom has a particular rate constant for reaction with methyl in the alkene as well as in the alkane series. Secondly, that the changes in reactivity are due to changes in the A factor and not in

⁵⁹ *Discuss. Faraday Soc.*, 1951, **10**, 35; for a different view cf. Leigh and Szwarc, *J. Chem. Physics*, 1952, **20**, 407.

activation energy, as was the case with the alkanes. No explanation for this most interesting fact has yet been advanced.

No other series of compounds has been investigated thoroughly apart from the cyclanes, where the variations are of a different kind from those previously considered. It is noteworthy that the variations in rate found among the cyclanes had been previously predicted by Brown⁶⁰ by consideration of the strains involved in the molecule and in the transition state. It is possible, however, that other attractive explanations could be found.

TABLE 6. *Rate constants at 182° C and frequency factors per hydrogen atom characteristic of different types of hydrogen atoms in alkenes (both in mole⁻¹ c.c. sec.⁻¹)*

Type of hydrogen atom	10 ⁻⁶ k/H	10 ⁻¹⁰ A/H
Primary . . .	4, 5, 4, 6	2
Secondary . . .	17, 18	7
Tertiary . . .	53	23

From the results in Table 4 as a whole, three facts stand out. First, that the spread of activation energies is small, only 8 kcal./mole, whereas the spread of C-H bond strengths is between the weakest bond in toluene and that in methane. Secondly, the general rule that primary hydrogen atoms react less readily than secondary, and these in turn less readily than tertiary, holds throughout, as shown by the values of the rate constant/number of "active" hydrogen atoms for each class of compound in Table 7.

TABLE 7. *Rate constants characteristic of various types of hydrogen atom in different classes of compound*

Class of compound :	Alkane	Alkene	Alkyne	Ether	Alcohol
Type of hydrogen atom	10 ⁻⁶ k/H at 182° C (mole ⁻¹ c.c. sec ⁻¹ /atom)				
Primary	0.3	5	7	1.5	2
Secondary	2.1	17	38	—	10
Tertiary	15	53	—	19	31

Thirdly, although there is a considerable variation in the *A* factors, yet they all, except for two doubtful cases, lie in the range 10^{10.4} — 10^{12.5} as is shown by Fig. 2. This means that the steric factors lie between 10⁻² and 10⁻⁴. The figures show that the concept of reactivity as applied to free-radical reactions is very vague when studies have only been made at one temperature. Whenever possible, activation energies and *A* factors should be determined, and if this cannot be accomplished, great caution should be exercised in interpreting the results.

The rates of three reactions of methyl radicals relative to the rate of

⁶⁰ *J. Amer. Chem. Soc.*, 1951, **73**, 212.

reaction (4) (p. 204) have been studied. The method (described in the section on methods) was first used by Anderson and Kistiakowsky⁶¹ and later by Williams and Ogg.⁶² The later work was considerably more



extensive and involved the determination of the relative rates of reactions

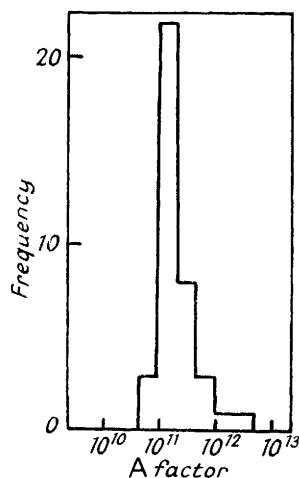


FIG. 2
The frequency of occurrence of *A* factors for methyl-radical reactions.

(4) and (8), where X is Cl, Br or I, over a range of temperatures. Thus $E_8 - E_4$ and A_8/A_4 were found; the values are given below:

Reaction	$E_8 - E_4$, kcal/mole	A_8/A_4
$\text{CH}_3 + \text{HI}$	0.75	0.23
$\text{CH}_3 + \text{HBr}$	0.95	0.13
$\text{CH}_3 + \text{HCl}$	2.4	0.04

Williams and Ogg considered that "hot" methyl radicals were involved in the reaction with hydrogen chloride, so the meaning of the figures is doubtful. For this reason the results cannot be directly compared with those obtained from the photolysis of acetone in the presence of hydrogen chloride.⁵⁶ The experiments are very difficult to conduct and to interpret, so little reliance should be placed upon the precise numerical values obtained. The supposition that reaction (4) takes place on every collision is reasonable but not proven.

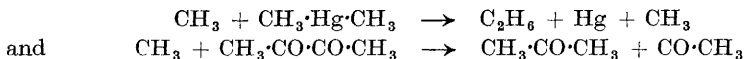
Large numbers of other gas-phase reactions of methyl radicals involving hydrogen abstraction have been postulated but not quantitatively investigated. Steacie¹ lists many of these.

No metathetical reactions of methyl in the gas phase have been quantitatively investigated in which atoms other than hydrogen are abstracted, though these certainly occur. Of particular importance are the reactions with the halogens which occur so rapidly that they cannot be studied by present techniques.

⁶¹ *J. Chem. Physics*, 1943, **11**, 6.

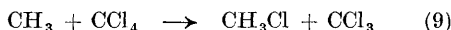
⁶² *Ibid.*, 1947, **15**, 696.

Two reactions have been found in which a methyl radical extracts a radical from a molecule. They are



The rate constant of the first is approximately represented by the equation $k = 10^7 e^{-1000/RT}$ and of the second by $k = 4.8 \times 10^{10} e^{-5600/RT}$ mole⁻¹ c.c. sec.⁻¹. Reactions of this type seem to be very rare and until more are found it is not possible to state with what sort of molecules they are likely to occur.

No methyl-radical reactions have been investigated in solution sufficiently fully to determine rate constants. Indeed, apart from the greater analytical difficulties, it is to be expected that in many cases complications may be caused by the fact that two methyl radicals released as a pair from a molecule by photolysis (as in the case of acetone and dimethylmercury) may be caged in and have a greater probability of combining than would be expected from the overall concentration of methyls and the rate constants in the gas phase, so that the rate of formation of ethane is not a reliable guide to radical concentration. Edwards and Mayo¹³ have investigated the rates



of a number of reactions of type (1) relative to the rate of reaction (9) at 100° c. The radicals were produced by pyrolysis of acetyl peroxide, and the reactions were followed by the relative rates of production of methane and methyl chloride. The rate constants k_1/k_9 in solution are compared in Table 8 with the rate constants, k_1 , determined by Trotman-Dickenson and Steacie⁴⁴ for the five compounds common to the two investigations (the k_1 value for oct-1-ene was assumed equal to $k_{\text{pent-1-ene}} + k_{n\text{-pentane}} - k_{\text{ethane}}$). The table shows a remarkable parallelism between the two sets of data: *cyclohexane* apart, the constancy of the last column is much

TABLE 8. *Relative rate constants for the reactions of methyl radicals in the gas phase and in solution*

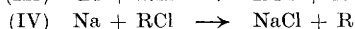
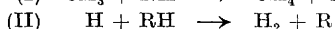
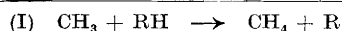
Compound	$\frac{k_1/k_9}{\text{(solution)}}$ at 100° c	$10^{-6}k_1$ (gas) at 100° c, mole ⁻¹ c.c. sec. ⁻¹	$\frac{10^{-6}k_1 \text{ (gas)}}{k_1/k_9 \text{ (solution)}}$
Benzene	0.04	0.091	2.3
Acetone	0.40	1.0	2.5
Toluene	0.75	1.9	2.5
Oct-1-ene	3.2	7.7	2.4
<i>cyclohexane</i>	4.5	3.4	0.8

better than the reliability of the figures would lead one to expect. The result is of importance because it is the first case in which a free-radical reaction has been accurately studied in the gas phase and in solution. However, there is some evidence that the reacting species in Mayo's work is not a methyl radical at all but the $\text{CH}_3 \cdot \text{CO} \cdot \text{O}$ radical. This difficulty is characteristic of reactions in solution.

The metathetical reactions of other radicals or atoms have been very little investigated in the gas phase or in solution. In Table 9 are collected the data on some of the other metathetical reactions in the gas phase which may be compared with the methyl reactions. The information is fragmentary, but as far as it goes it leads us to suppose that the gradations in the reactivity of methyl radicals with various compounds will be reflected in the reactivity of other radicals with the compounds. On the other hand, there are some notable exceptions to this rule, and even for the reactions presented in the table there exist data which conflict with this conclusion. In solution the transfer-reaction velocity constants which have been measured for the thermal polymerisation of styrene in various solvents⁶³ correspond to metathetical reactions of the polystyrene radicals. In this case, where an extreme difference in molecular size is involved, there appears to be little correlation with the methyl reactions.

TABLE 9. *Activation energies (in kcal./mole) of various metathetical reactions*

R	Reaction							
	I	Ref	II	Ref	III	Ref.	IV	Ref
H	10	64	5	65	17.6	67	6.1	70
CH ₃	12.8	64	13	66	18.3	68	10.0	70
C ₂ H ₅	10.4	64	9	66	13.6	69	9.4	70
Bu ^s	8.3	64	7.2	66	—	—	8.6	70
Bu ^t	7.6	64	6.3	66	—	—	7.8	70
CH ₂ :CH·CH ₂	7.7	64	5.0	66	—	—	5.3	70
CH ₃ ·CH:CH·CH ₂	7.7	64	5.0	66	—	—	—	—



Addition Reactions of Methyl Radicals.—Large numbers of addition reactions of methyl radicals of the type $\text{CH}_3 + \text{X}=\text{Y} \rightarrow \text{CH}_3\text{-X-Y}$ have been identified, with a wide variation of the groups X and Y. A list of these types is given below. For only one addition reaction, however,

Type of multiple bond	Example	Type of multiple bond	Example
C=C	Many alkenes	C=O	Carbon monoxide
C≡C	Ethyne	N=N	Azomethane
C—C—C—C	Butadiene	O—O	Oxygen

has the velocity constant been determined, *viz.*, for $\text{CH}_3 + \text{O}_2 \rightarrow \text{products}$. Marcotte and Noyes⁷¹ found the rate constant for this reaction by com-

⁶³ Burnett, *Quart. Reviews*, 1950, **4**, 292.

⁶⁴ See Tables 3 and 4.

⁶⁵ Farkas and Farkas, *Proc. Roy. Soc.*, 1935, **A**, **152**, 124.

⁶⁶ Darwent and Roberts, *Discuss. Faraday Soc.*, 1953, **14**.

⁶⁷ Bodenstein and Lütkemeyer, *Z. physikal. Chem.*, 1935, **114**, 208.

⁶⁸ Kistiakowsky and Van Artsdalen, *J. Chem. Physics*, 1944, **12**, 469.

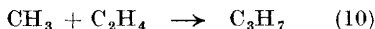
⁶⁹ Anderson and Van Artsdalen, *ibid.*, p. 479

⁷⁰ Warhurst, *Quart. Reviews*, 1951, **5**, 44.

⁷¹ *J. Amer. Chem. Soc.* 1952, **74**, 783.

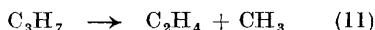
paring the rate of disappearance of oxygen from an illuminated acetone-oxygen mixture with the rate of production of methane. They found the activation energy of the reaction to be 0 ± 0.5 kcal./mole and that $A = 8 \times 10^{10}$ mole⁻¹ c c. sec.⁻¹.

The reason why it has been impossible to determine the velocity constant of reaction (10) is that the propyl radical rapidly reacts with another



ethene molecule, combines or disproportionates with a methyl, propyl, or higher radical, or, at temperatures above 520° K, decomposes at an appreciable rate. The situation is thus extremely complicated and cannot be sorted out by our present techniques. An attempt has been made⁷² to give a general kinetic treatment of the reactions which occur when acetaldehyde is photolysed in the presence of a number of different alkenes. No reliable rate constants for the individual steps have been derived by this method, and the study illustrates clearly the great difficulties which have to be overcome before quantitative results can be obtained by this straightforward approach.

Some information about the addition of methyl radicals to alkenes may be obtained indirectly by studying the kinetics of the reverse reaction. Thus although it has not been possible to determine the activation energy of (10), yet the activation energy of the reverse reaction (11) can be measured.



This has been done by Bywater and Steacie,^{3, 4, 5} who produced the propyl radicals by mercury photosensitisation. They found $E = 20$ kcal./mole. If the $\text{C}_3\text{H}_7\text{-H}$ and $\text{CH}_3\text{-H}$ bond strengths are known, it is possible to calculate ΔH for reaction (11) from well-established thermochemical data. The data due to Stevenson⁴⁵ on the $\text{CH}_3\text{-H}$ and primary, secondary, and tertiary C-H bonds, which have been referred to above, can be used for this purpose. Hence $\Delta H = 23$ kcal.

Now $\Delta H = E_{11} - E_{10}$, therefore $E_{10} = -3$ kcal.

In Table 10 all the information is set out which can be calculated in this way from the published data for the addition of hydrogen atoms or methyl or ethyl radicals to alkenes. All the data on the decomposition of the

TABLE 10. *Activation energies (kcal./mole) for the addition of radicals to alkenes*

Alkene radical	Hydrogen atom	Methyl radical	Ethyl radical
Ethene	+ 2	- 3	+ 2
Propene	+ 1, (+ 4)	- 1, (+ 2), - 3	-
2-Methylpropene	- 1, (- 8)	-	-

radicals come from the papers by Bywater and Steacie; Stevenson's bond strengths⁵⁹ have been used. When the decomposition mechanism assumed

⁷² Raal, Danby, and Hushelwood, *J.*, 1949, 2225.

involves the internal rearrangement of one of the fragments, the result is placed in parentheses as being of doubtful value. The results in the table are uncertain to about ± 4 kcal., so the only conclusion which can be drawn is that these addition reactions have very small activation energies.

The entropy change in the equilibrium formed by reactions (10) and (11), for example, can be calculated with a reasonable degree of confidence because most of the uncertainties due to our lack of knowledge of the properties of the radicals occur on both sides of the equilibrium. So if A_{11} and E_{11} are known we can calculate A_{10} and E_{10} from bond-strength and thermodynamic data. Thus we find⁷³ that the additions of methyl radicals to ethylene and propene have frequency factors of the order of 10^6 mole⁻¹ c.c. sec.⁻¹. This remarkable conclusion is supported by the fact that similar calculations for the reactions of hydrogen atoms give results which are in good agreement with the measured rates.

⁷³ Trotman-Dickenson, *Discuss. Faraday Soc.*, 1953, **14**.