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EXPERIMENTAL METHODS OF DETERMINING THE ACTIVATION ENERGIES OF ELEMENTARY REACTIONS¹

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¹ This paper was presented in part at the Symposium on the Activation Energies of Elementary Reactions, which was held under the auspices of the Division of Physical and Inorganic Chemistry at the 102nd Meeting of the American Chemical Society, Atlantic City, New Jersey, September, 1941.

I. INTRODUCTION

The present discussion will be limited to those elementary reactions which involve the participation of atoms and free radicals of short life, and which occur in the gas phase. Such elementary reactions are very frequently assumed as intermediate steps in the mechanism of thermal and photochemical processes. It is therefore of obvious importance to investigate their rates by independent means. Unfortunately, the short life of the substances involved makes ordinary methods of investigation impossible, and thus necessitates the use of rather indirect methods of attack. This arises from a number of causes: (a) It is impossible to prepare substances of such short life in high concentration, or in a state of purity. As a result the atoms or radicals must usually be prepared *in situ*, in the presence of a very large excess of other substances. (b) On account of the short life of the active substances, their estimation and identification are difficult. (c) The products of an elementary reaction often include other substances of short life. These substances react further, and it is often very difficult to disentangle the primary process from such secondary reactions. (d) The methods of preparing atoms and radicals often produce several active species simultaneously; hence numerous side reactions may occur which mask the process under investigation.

To make an unequivocal determination of the activation energy of an elementary reaction the following information is necessary: (a) what atoms or radicals are produced by the method employed; (b) the concentrations of the atoms or radicals and of other substances; (c) the amount of product produced in a definite time, and the identity of the product; (d) the effect of temperature on (a), (b), and (c); (e) the occurrence of secondary or side reactions, and their rates, temperature dependence, etc.

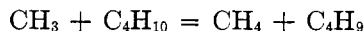
There is no question that up to the present no investigation of an elementary reaction has yielded direct and accurate information on all the above points. As a result, information on the activation energies of elementary reactions comes from a knowledge of one or more of the above factors, together with inference from analogous cases, etc., in place of the deficient information. The results are therefore, as Kassel puts it, "tainted with contingency." However, as information accumulates, more and more confidence can be placed in the values assigned to the simpler reactions, and reliable information is steadily forthcoming.

It may be pointed out (*cf.* Rice (242)) that we are primarily interested in the activation energies of four main types of process: (1) the rupture of a bond in a stable molecule, leading to the formation of atoms or radicals; (2) reactions between atoms or radicals and molecules; (3) reactions between two atoms or radicals; and (4) the decomposition of radicals.

Virtually all the estimates of activation energies have been made by one of the following procedures:

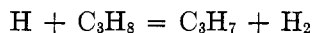
(a) *The rate of production of the product is measured as a function of temperature.* For example, the photolysis of mercury dimethyl leads to the production of

methyl radicals. In the presence of butane, methane is formed. This is assumed (278) to be due to the occurrence of the reaction



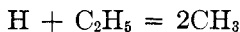
By measuring the rate of formation of methane as a function of temperature, we can thus arrive at the activation energy of this reaction.²

(b) *The rate of disappearance of the reactant is measured as a function of temperature.* Thus the reaction



is followed by determining the rate of disappearance of propane in a system containing propane and hydrogen atoms (292).

(c) *The value of the activation energy is obtained by an analysis of the mechanism of a complex change.* Thus we may make an approximate estimate of the activation energy of the reaction



from an analysis of the mechanisms of various reactions involving ethane and hydrogen atoms (295, 296, 324).

(d) *The activation energy is obtained from the rate of reaction at one temperature, together with suitable assumptions about the frequency factor.* This method is very frequently employed.

(e) *The lower or upper limit to the value of the activation energy is obtained by the appearance or non-appearance of the reaction under certain conditions.* Thus hydrogen atoms do not react with methane at room temperature in a contact time of 1 sec., so that it may be concluded that the activation energy is not less than 10 kcal. (98). In such cases there is always the danger that the non-occurrence of the reaction is due to a low frequency factor, rather than to a high activation energy.

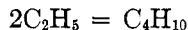
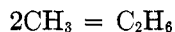
(f) *The relative values of the activation energies of two reactions may be inferred by assuming equal frequency factors (or by assigning different values to them on the basis of steric or other considerations) and comparing the amounts of products formed.* Thus in the photolysis of methyl ethyl ketone equal amounts of methyl and ethyl radicals are presumably formed. Since the amounts of ethane, propane, and butane obtained as products are roughly those estimated from

² In this, and in practically all other cases, the activation energy is calculated from the Arrhenius equation

$$k = Ae^{-E/RT}$$

assuming A to be temperature independent. While this is not strictly true, it introduces no appreciable error with the accuracy attainable. In other words, for the present purpose we may assume the Arrhenius equation to be an experimental fact.

probability considerations (174), it may be concluded that there is little difference in the activation energies of the three recombination reactions



(g) *The activation energies of part reactions are obtained by comparing an assumed mechanism with experiment.* This method has been widely used by Rice (242).

(h) *The result is obtained by inference from thermal data and bond strengths.*

(i) *The result is obtained from a knowledge of the activation energy of the reverse reaction, and of the heat of reaction.* In practice the main difficulty here is that we rarely know the heats of elementary reactions with any degree of accuracy.

(j) *Theoretical methods.* These are beyond the scope of the present review.

II. EXPERIMENTAL METHODS

In general, the two characteristic features of any experimental method are (A) the means of producing the active species, and (B) the method by which they are estimated. In the following pages we shall discuss these two questions in detail separately, together with a description of the main combinations of the two which have been used in practice. Ordinary methods which are used for the investigation of reactions of stable substances will not be discussed here.

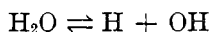
A. THE METHODS OF PRODUCING ATOMS AND RADICALS

1. Thermal

(a) Active species in thermal equilibrium with the substance from which they are produced

In the case of the common diatomic molecules, sufficient information exists to enable the degree of dissociation to be calculated precisely at all temperatures. Table 1 gives the temperatures corresponding to various amounts of dissociation when the pressure of the gas is 1 mm. (91). It will be seen from the table that at room temperature the alkali metals are appreciably dissociated into atoms; at moderate temperatures iodine is as well. With most other diatomic molecules, however, very high temperatures must be reached before the atom concentration becomes appreciable.

Definite information about the dissociation of more complex molecules has been obtained experimentally in a few cases. For example, Bonhoeffer and Reichardt (37) made a spectroscopic investigation of the dissociation of water vapor, and determined the equilibrium for the reaction



In general, this method is of little use in the production of free radicals by the thermal decomposition of organic molecules. The strengths of the bonds in

organic molecules are still a matter of controversy. The values given by a number of workers are listed in table 2, and a very consistent and plausible set recently given by Baughan, Evans, and Polanyi is shown in table 3. It is evident that, whatever the true values may be, they are so high that, except possibly in the case of the iodides, the equilibrium concentration of free radicals or atoms is far too small to be of importance except at temperatures so high that secondary reactions come into play and make the situation extremely complex. As a result, little use can be made of the stationary-state concentration of free radicals in equilibrium with organic molecules, and the method has not been widely used, except in a few special cases. The main examples of

TABLE 1
Dissociation of diatomic molecules (from Geib (91))
Pressure = 1 mm.

SUBSTANCE	HEAT OF DISSOCIATION	TEMPERATURE AT WHICH THE DEGREE OF DISSOCIATION IS		
		1 per cent	0.01 per cent	0.0001 per cent
	<i>kcal.</i>	<i>°K.</i>	<i>°K.</i>	<i>°K.</i>
K ₂	11.8	270		
Na ₂	17.0	390	280	
Li ₂	26.7	590	420	330
I ₂	35.2	680	510	410
Br ₂	45.2	850	640	510
Cl ₂	56.9	1040	800	640
HI.....	70	1310	975	780
HBr.....	86.7	1590	1200	965
HCl.....	101.5	1830	1380	1115
H ₂	102.7	<u>1910</u>	1425	1140
D ₂	104.6	1920	1440	1160
S ₂	102.6	1930	1430	1140
O ₂	117.4	2000	1530	1240
P ₂	115	2200	1620	1260
NO.....	122.5	2100	1600	1290
CO.....	160 (?)	2580	1990	1620
N ₂	170	2850	2200	1800

its use in connection with the investigation of elementary reactions are: (1) reactions involving atomic hydrogen; (2) reactions involving atomic sodium; (3) reactions involving potassium, magnesium, cadmium and zinc atoms; and (4) reactions involving iodine atoms.

(1) *Reactions involving atomic hydrogen:* The thermal conversion of para- to ortho-hydrogen was investigated by Farkas (69, 70) at temperatures in the range 600° to 750°C. The reaction was of the 3/2 order, indicating the mechanism

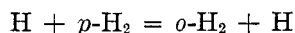
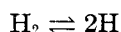


TABLE 2
The strength of bonds in organic molecules (from Rollefson and Burton (254))

BOND	STRENGTH	REFERENCE
	<i>kcal.</i>	
C—C.....	82.5 (hydrocarbons)	(242)
	83	(204)
	84.2 (paraffins)	(205)
	110-115	(169, 170)
	71	(68)
	97.6	(324)
	72.1 (ethane)	(41)
	89.5 (ethane)	(179)
C=C.....	162 (ethylene)	(179)
	145 (hydrocarbons)	(242)
	149	(204)
	200	(169, 170)
	125	(68)
	151.2 (olefins and cyclic compounds)	(205)
C≡C.....	198.5 (acetylenic hydrocarbons)	(205)
	220.5 (acetylene)	(179)
	200	(204, 242)
	187	(218, 219)
C—H.....	100 (hydrocarbons)	(242)
	92.3	(176)
	94.8 (methane)	(41)
	100 (methane)	(205)
	92	(68)
	114	(169, 170)
	102.5	(199, 200)
	108	(324)
	103 (methane)	(179)
C—O.....	92	(68)
	82 (alcohols, ethers)	(242)
	81.8	(204)
	83 (aliphatic ethers)	(205)
	81 (aliphatic primary alcohols)	(205)
C=O	178 (formaldehyde)	(179)
	183.5 (acetone)	(179)
	188	(68)
	177.8 (ketones)	(205)
	166.1 (formaldehyde)	(205)
	174.4 (other aldehydes)	(205)
C—Cl.....	78 (alkyl halides)	(242)
	73	(68)
	71	(99)
C—Br.....	65.3	(204)
	58	(99)

TABLE 2—*Concluded*

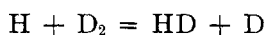
BOND	STRENGTH	REFERENCE
	<i>kcal.</i>	
C—I.....	56.5	(204)
	44	(68)
C—N.....	64.2 (methylamine)	(179)
	66 (amines)	(242)
	68.4 (amines)	(205)
C≡N.....	200 (nitriles, HCN)	(242)
	202 (HCN)	(205)
	209.2 (aliphatic cyanides)	(205)
	207.5 (HCN)	(179)

TABLE 3

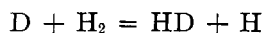
Estimates of bond strengths by Baughan, Evans, and Polanyi (15a)

R	BOND STRENGTHS			
	R—H	R—I	R—CH ₃	R—OH
	<i>kcal.</i>	<i>kcal.</i>	<i>kcal.</i>	<i>kcal.</i>
CH ₃	103.6	55.0	88.2	87.6
C ₂ H ₅	96.4	51.2	83.4	86.2
<i>n</i> -C ₃ H ₇	95.5	50.7	82.8	86.7
<i>iso</i> -C ₃ H ₇	91.0	48.4	80.2	86.5
<i>tert</i> -C ₄ H ₉	86.9	46.3	76.9	87.6

In a similar way, Farkas and Farkas (73) investigated the thermal conversion of ortho- to para-deuterium, and the reactions



and



There seems to be no doubt that in all these cases the reaction proceeds through the agency of the stationary concentration of hydrogen or deuterium atoms in thermal equilibrium with undissociated molecules.

The thermal reactions of deuterium with methane, ammonia, and water also appear to proceed through the agency of the equilibrium concentration of deuterium atoms (72, 75). However, it is only with exceptionally stable substances, such as ammonia, methane, and water, that this method can be used to investigate the hydrogen-atom reactions, since with most substances the high temperatures necessary would result in decomposition and other complications.

(2) *Reactions involving atomic sodium:* As we have seen, sodium, even at room temperature, is appreciably dissociated, and at 200° to 300°C. it is mainly

in the atomic state. The reactions of sodium with many substances have been investigated by Polanyi and his coworkers by two rather similar methods. The so-called method of dilute flames is a modification of the flow method (see section (b) (1) on page 236) which is suitable for the investigation of very fast atomic reactions.

The original form of the method, that of "highly dilute flames," is as follows (20, 21, 22, 27, 214): Two reactants, A and B, are led into a tube from opposite ends. The pressures are so low that the mean free paths are greater than the diameter of the tube. Under these circumstances the gases mix solely by diffusion. As A penetrates into B it is consumed, and its pressure sinks to zero. Similarly with B, as it penetrates into A. We thus have the state of affairs shown in figure 1. The curve U represents the product $P_A P_B$, and should thus be proportional to the rate of reaction if the reaction is bimolecular. The essential feature of the method is the determination of the rate of reaction from the

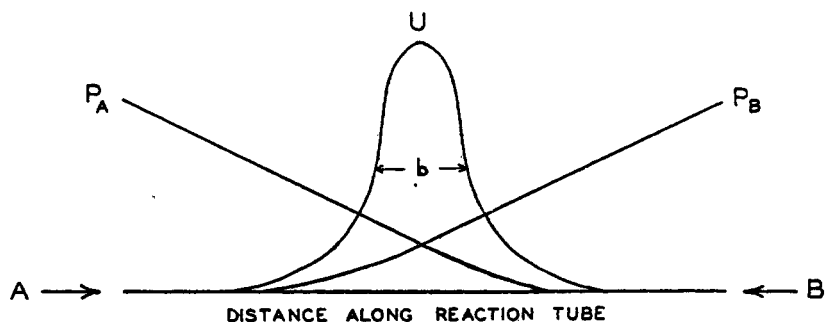


FIG. 1. The method of highly dilute flames. Curve showing consumption of reactants and formation of product as a function of distance along the reaction tube.

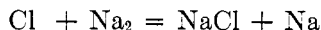
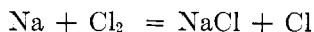
breadth of the curve. It is obvious that a relationship should exist, since the slower the reaction the farther the reactants will penetrate into one another. The exact relation is

$$k = \frac{27}{b^3} \frac{1}{2qUk_A k_B}$$

where k is the rate constant of the reaction, k_A and k_B are the diffusion resistances of the two gases, q is the cross section of the tube, and b is the "half-breadth" of the curve U . The form of the curve is easily obtained if the product of the reaction is a solid. Thus in the reaction between sodium and chlorine, the curve can be obtained from the thickness of the sodium chloride deposit at any point. This can be obtained by direct weighing or by opacity measurements.

By a determination of the over-all rate constant in this way, together with an examination of the luminescence accompanying the reaction, Polanyi and his collaborators have obtained information about the rates of many reactions

involving metal atoms, and incidentally about reactions of halogen atoms, etc.; e.g., the reactions



For a review of this work see Polanyi (214).

A modification of this method is that of "diffusion flames." This is suitable for reactions somewhat slower than those considered above, i.e., for those with an activation energy of a few kilocalories (118, 119, 120, 123, 171). This method is similar to the dilute-flame method, in that the rate of reaction is inferred from measurements of the distance which one component penetrates into the other before being used up. To make this distance shorter so that slow reactions can be investigated, a foreign gas at a pressure up to 10 mm. is added. This slows

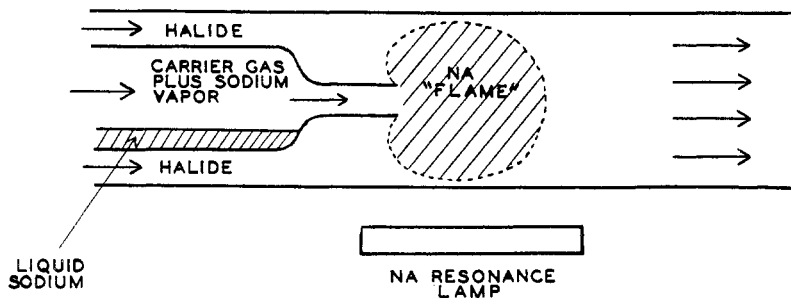


FIG 2. The method of diffusion flames

down diffusion and acts as a carrier for the reactants. The apparatus is illustrated in figure 2.

One reactant, say sodium vapor, together with an inert gas as carrier enters through a jet into a chamber containing the other reactant, say methyl chloride. The partial pressures of the reactants are of the order of 2×10^{-3} mm. for sodium, and 0.02 to 0.5 mm. for the alkyl halide. By illuminating the sodium vapor with a resonance lamp giving the D doublet, it is possible to make the sodium vapor visible. We can thus measure the size of the "flame" to a distance at which the concentration of sodium vapor is so low that it cannot be detected by this method. We can then calculate the rate constant of the reaction from the size of the flame, or zone of penetration of one reactant into the other, by means of considerations similar to those used in the case of the dilute-flame method.

Experimentally the conditions are adjusted so that for simplicity (1) the size of the flame is smaller than the tube diameter, and wall effects are thus eliminated, (2) the rate of flow of carrier gas in the jet is fast enough so that no appreciable back-diffusion of the reactant against the sodium stream occurs, and

(3) the flow of the reactant and its amount are so arranged that its concentration is constant throughout the tube, and is not appreciably affected by the flow of carrier gas, or by reaction. (It is always present in large excess compared with sodium.)

In practice, the partial pressure of the reactant is varied until a certain size of flame is produced. It is evident that the slower the reaction rate, the higher will be the necessary partial pressure. Thus with methyl iodide, where reaction occurs at approximately every collision, 10^{-3} mm. is sufficient, while with methyl fluoride even with a pressure of 10 mm. the reaction is so slow that the whole tube is full of sodium vapor, i.e., less than one collision in 10^6 is effective. In general, the suitable range of reactions the rates of which can be measured are those in which from 1/10 to 1/100,000 of the collisions between the reactants are effective.

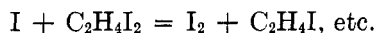
Polanyi and his coworkers have investigated a whole series of reactions by this method, all of them involving metal atoms and halides: e.g.,



The absence of luminescence from the reactions results in it not being possible to obtain as much information about secondary reactions as is the case with the dilute-flame method. It has, however, proved possible to make accurate measurements of the activation energies of numerous metal atom-halide reactions (214).

(3) *Reactions involving potassium, magnesium, cadmium, and zinc atoms:* The situation here is the same as that for sodium (214).

(4) *Reactions involving iodine atoms:* The thermal decomposition of ethylene iodide is strongly catalyzed by iodine, and the rate is proportional to the square root of the iodine concentration (8, 216, 263). There seems to be no doubt that we have the reactions



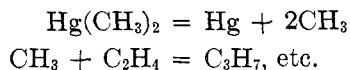
It is known that I_2 catalyzes a large number of decompositions, possibly through the intermediate formation and decomposition of an alkyl iodide. (See reference 262 for a review of catalysis by iodine.)

(b) Production of active species by thermal decomposition

Atoms or radicals are produced in the thermal decomposition of many substances. The methods by which advantage is taken of this fact in practice are numerous, and differ mainly in the time during which the reactant remains in the heated zone.

(1) *The static and flow methods:* Using the ordinary static and flow methods, atom or radical reactions can be investigated by mixing a substance, the sensitizer, with the reactant and heating the mixture to a temperature at which the reactant is normally stable, while the sensitizer decomposes with the formation of atoms or radicals. The first investigation of a sensitized reaction of this kind

was that of Taylor and Jones (312), who investigated the decomposition of mercury and lead alkyls in the presence of hydrogen and ethylene. They found that the main result was polymerization of the ethylene, pointing to the occurrence of the following reactions:



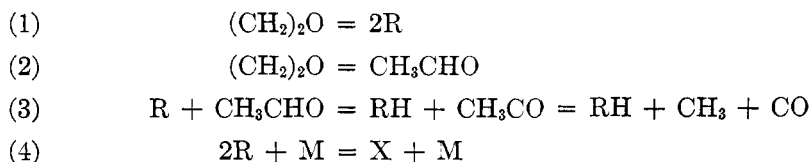
In order to apply the method in such a way as to obtain quantitative information, it is essential to know the kinetics of the decomposition of the sensitizer, and especially the radicals formed in its decomposition. As a result, the sensitizers which have been at all widely used are comparatively few in number. The main ones are ethylene oxide, azomethane, acetone, and metal alkyls.

The decomposition of *ethylene oxide* was first investigated by Heckert and Mack (121) in the temperature range 380° to 444°C. They showed that the reaction was of the first order, the rate at high pressures being given by

$$k_\infty = 6.3 \times 10^{14} e^{-52000/RT} \text{ sec.}^{-1}$$

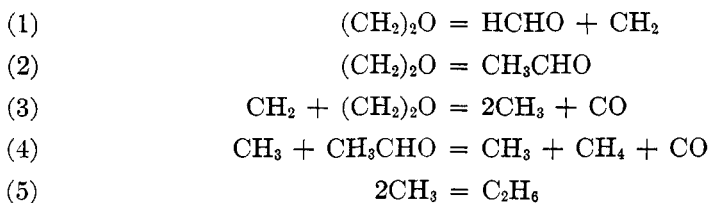
The products were approximately 50 per cent carbon monoxide, 36 per cent methane, 7 per cent ethane, and 7 per cent hydrogen.

The mechanism of the reaction was discussed by Sickman (269). He concluded that the complexities of the reaction could be explained on the assumption that the mechanism is as follows:



where R represents a free radical, X a molecule, and M is any third body. All the experimental facts are readily interpreted on this basis if we assume that k_1 is much smaller than k_2 , i.e., that most ethylene oxide molecules isomerize to acetaldehyde, which then undergoes a radical-sensitized decomposition, and that relatively few ethylene oxide molecules give free radicals by reaction 1. It should be noted that the sensitized decomposition of acetaldehyde will not affect the radical concentration, since each radical removed by reaction 3 is regenerated.

Fletcher and Rollefson (79, 81) reinvestigated the reaction with special emphasis on the rôle of free radicals. Their work led them to postulate a mechanism of the type suggested by Sickman, but of a more detailed nature:



This mechanism is in good agreement with their rate measurements, analyses for formaldehyde and acetaldehyde, etc. By assuming that all the hydrogen found in the products comes from the decomposition of formaldehyde formed by reaction 1, and that all the ethane comes from reaction 5, they calculate that 14 per cent of the ethylene oxide decomposes by reaction 1. Whence, since each methylene gives rise to two methyls, they calculate that 0.3 methyl is formed for each ethylene oxide molecule decomposed.

While it cannot be said that this mechanism is established, it is undoubtedly plausible, and all the evidence indicates that by no means all the ethylene oxide decomposes by way of free radicals. It seems very unlikely that Fletcher and Rollefson's estimate of the fraction of ethylene oxide molecules giving rise to radicals is too low, although it may well be too high, since hydrogen and ethane may arise in other ways.

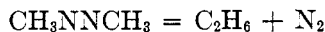
Many investigations have been made using ethylene oxide as a sensitizer (58, 79, 80, 81, 121, 287). The production of carbon monoxide has usually been used as an indication of the amount of decomposition of ethylene oxide, and hence of the number of methyl radicals generated in the system. It should, however, be noted that there is a possibility, especially when ethylene oxide is present in small quantity, that reactions involving methylene may be important.

Thus, Echols and Pease (58) investigated the ethylene oxide-sensitized decomposition of a number of paraffins by mixing the paraffin and ethylene oxide at temperatures around 400°C., allowing the ethylene oxide to decompose, and then analyzing the products for unsaturates and carbon monoxide. On the assumption that all the unsaturates come from the paraffin and all the carbon monoxide from the ethylene oxide decomposition, the ratio C_nH_{2n}/CO is a measure of the chain length of the sensitized decomposition. Thus at 425°C. with an 8:1 mixture of *n*-butane and ethylene oxide, they found

$$C_nH_{2n}/CO = 12.0$$

Hence, if we assume 0.3 methyl is formed for each molecule of decomposing ethylene oxide, we obtain a chain length of about forty. It may be noted that, irrespective of any uncertainty about the mechanism of the ethylene oxide decomposition, these results definitely indicate that chains are set up, since even with the extreme, and unlikely, assumption of two radicals from each molecule of ethylene oxide decomposed, the chain length would still be at least six.

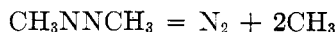
Much work has been done on the reaction involving *azomethane*, so that here we shall merely outline the main findings. (For an extended discussion see Schumacher (262).) The main over-all reaction in the azomethane decomposition is (224)



Small amounts of other products are also formed. The reaction is a classical example of a unimolecular change, the limiting high-pressure rate constants being given by

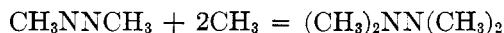
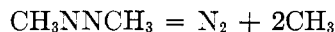
$$\begin{aligned} k_\infty &= 3.13 \times 10^{16} e^{-52500/RT} \text{ sec.}^{-1} \quad (\text{Ramsperger}) \\ &= 8 \times 10^{15} e^{-50200/RT} \text{ sec.}^{-1} \quad (\text{Rice and Sickman (249, 271, 272)}) \end{aligned}$$

It has been shown in a number of cases, examples of which are given later, that decomposing azomethane can induce the decomposition of other substances. This suggests that the decomposition process proceeds by way of free radicals, i.e.,



Experimental proof that at least part of the decomposition proceeds in this manner comes from the work of Leermakers (154) and of Rice and Eving (231), who showed that mirrors were removed when azomethane was decomposed by the usual Paneth-Rice technique. The evidence favors the idea that while azomethane decomposes by a free-radical mechanism, it does not do so by a chain mechanism (see 82, 122, 155, 227). Thus Leermakers found that at 275°C. ethyl radicals did not react with azomethane. Also, up to 260°C. the quantum yield of the photodecomposition is approximately 2; hence no long chains are set up by the methyl radicals produced in the primary process.

Taylor and Jahn (308) have recently reinvestigated the decomposition with emphasis on the analytical aspects of the problem. They conclude that the mechanism is



the ethane arising by secondary reactions. They find

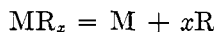
$$k_\infty = 3.51 \times 10^{16} e^{-52500/RT} \text{ sec.}^{-1}$$

in good agreement with previous work. On the basis of their mechanism, the rate of decomposition of azomethane into methyl radicals will be only half this.

There are numerous cases of decompositions induced by radicals from azomethane. Examples are the following: the decomposition of butane, and the polymerization of acetylene, of ethylene, and of propylene (Rice and Sickman (272)); the decomposition of acetaldehyde (Allen and Sickman (3, 270)); the decomposition of divinyl ether (Taylor (307)); the decomposition of heptane (Maess (167)); the decomposition of methyl ethyl ether and of propylamine (Rice, Walters, and Ruoff (247)).

The *acetone* decomposition has been the subject of many investigations, and the general kinetics appear to be fairly well established (128, 131, 246, 335). There is considerable evidence which indicates that methyl radicals are formed in the decomposition (1a, 156, 200, 201, 236, 244). Leermakers (156) has used the acetone decomposition to induce the decomposition of dimethyl ether.

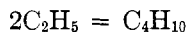
Methyl alkyls are by far the most important sensitizers. There seems to be little doubt that in all cases the mechanism of the decomposition is



where M is a metal and R is an alkyl radical. The above process presumably occurs in steps:



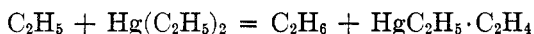
In interpreting the results of induced decompositions there are possible complications. For example, in the case of mercury diethyl, apart from the obvious secondary reactions,



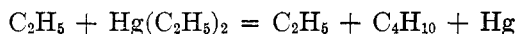
and



there is also the chance of

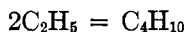
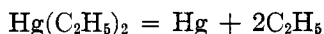


or



etc.

In general, however, there is no doubt that the main process is the simple formation of radicals, which then undergo secondary reactions. These substances have been used, for the most part, in two distinctly different ways for the investigation of radical reactions. In the one method a static system is used: the metal alkyl is decomposed in the presence of another substance and causes its induced decomposition. In the other method a flow system is employed: the metal alkyl is decomposed, and from the products obtained it is possible to draw conclusions regarding the relative rates of recombination and disproportionation reactions; *viz.*,



Information exists on the pyrolysis and photolysis of a large number of metal alkyls, and on their use as sensitizers, as indicated in table 4.

Various *other substances* have been used as sensitizers. Some examples follow: methyl ether (80); biacetyl (246a); ethyl ether (80, 82a); ethyl vinyl ether (325b); propane (127); butane (127); triphenylmethylazobenzene (261, 261a); silane (61); ethyl iodide (255a, 306a); ethyl bromide (255a); oxygen (158, 159, 160, 161, 162); products of paraffin decompositions (127); and tetraphenylsuccinic acid dinitrile (261a).

(2) *The Paneth-Rice method—very fast flow*: The method by which Paneth and Hofeditz (192) first discovered the free methyl radical is, in reality, only a very fast flow method. Since the main feature of this work is not the means by which radicals are produced, but rather the means used for their detection, the method is discussed in section B1 (page 255).

(3) *Methods using heated filaments*: The classical experiments of Langmuir were the first examples of this method (84, 150, 151, 152). Langmuir investigated the heat loss from metal filaments heated *in vacuo* or in the presence of hydrogen, oxygen, or other gases. The apparatus used was a more or less standard type of filament lamp bulb. He showed that at very high temperatures

hydrogen was dissociated into atoms on the filament, and that the atomic hydrogen thus produced reached the walls of the bulb at low pressures, where its activity was shown by the reduction of metallic oxides and by other reactions.

Considerable information on catalytic reactions has been obtained by this method, but in its ordinary form it is not of much assistance as far as homogeneous elementary reactions are concerned.

A modification of the method has been used by Storch (305). Storch wished to ascertain the initial products of the decomposition of methane, without complications due to secondary reactions. To accomplish this he decomposed methane at low pressures on a hot carbon filament in a "lamp-bulb" which was cooled in liquid nitrogen. The products thus condensed out immediately they

TABLE 4
Metal alkyls: pyrolysis, photolysis, and use as sensitizers

SUBSTANCE	REFERENCES		
	Pyrolysis	Photolysis	Use as sensitizer
Pb(CH ₃) ₄	(192, 275)	(157)	(15b)
Pb(C ₂ H ₅) ₄	(50, 155, 172, 195, 212)	(219a, 220, 320)	(51, 155, 156, 158, 274, 312)
Pb(C ₆ H ₅) ₄	(57, 196)	(157)	
Hg(CH ₃) ₂	(52)	(52, 61a, 165, 220, 278, 318, 320, 322)	(85, 244, 255, 278, 312, 318)
Hg(C ₂ H ₅) ₂	(312)	(174a)	(174a, 312)
Hg(C ₄ H ₉) ₂	(86, 196) -		
Hg(C ₇ H ₁₅) ₂	(240)		
Si(CH ₃) ₄	(124)		
Si(C ₂ H ₅) ₄	(326)		
Si(C ₃ H ₇) ₄	(326)		
Ge(C ₂ H ₅) ₄	(90)		
Sn(C ₆ H ₅) ₄	(86)		
Bi(CH ₃) ₃	(192)		
Zn(CH ₃) ₂	(192)	(320)	
Sb(CH ₃) ₃	(192)		

were formed. He showed that under these circumstances the first recognizable product was ethane.

The main use of the filament method in the investigation of elementary reactions is that of Belchetz and Rideal (16, 17, 18). They employed two different types of apparatus. In both of these the gas streamed through at a high velocity (*ca.* 100 cm. per second) and at 0.1 mm. pressure over a heated platinum or carbon filament. In the first apparatus any radicals formed by the decomposition of the gas on the hot filament were caught on a water-cooled target 3 mm. away from the filament. Mirrors could be deposited on this target, and any products formed were caught in a liquid-air trap. Since the distance between the filament and the target was so small, of the order of one mean free path, any radicals formed would reach the target without undergoing

collisions. We should thus definitely be able to detect the radicals without any possibility of secondary processes intervening.

In the second apparatus the mirror was on the wall of the reaction vessel opposite the filament. It was considerably farther from the filament than in the former case, and the system thus resembled the hot-tube type of apparatus employed by Paneth and by Rice.

With both sets of apparatus tellurium and iodine mirrors were used, and platinum and carbon filaments. Most of the work was done with carbon filaments.

We shall return to this method later in connection with the detection of radicals. It may be mentioned here, however, that there is a considerable possibility that complications are introduced by the presence of the carbon, and that the activation energies of the decomposition of substances into free radicals calculated from the results may refer to catalytic processes on the surface of carbon or platinum, rather than to the homogeneous split into radicals in the gas phase. Certainly in Langmuir's work the dissociation of hydrogen into atoms occurred in an adsorbed layer of the surface of tungsten, and not merely by the molecule acquiring energy on impact. By analogy there seems every reason to suspect that, for example, a hydrocarbon may be adsorbed on the carbon filament prior to dissociation into radicals. Indeed, theoretical considerations are overwhelmingly in favor of such an occurrence. Evidence that this is the case will be presented later in discussing the detection of radicals produced by the Belchetz-Rideal method.

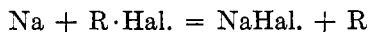
For a discussion of the production of hydrogen atoms by heated tungsten filaments, see Roberts and Bryce (251).

Haber and Oppenheimer (109) have used hydrogen atoms, produced by a hot filament, in a flow system to start sensitized explosions in hydrogen-oxygen mixtures at temperatures as low as 300°C. (see also 77, 108, 110).

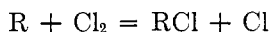
(c) Production of active species by reactions of higher order than the first

In addition to their production by thermal decomposition, radicals and atoms may arise as intermediate stages in thermal reactions of higher order. In some cases they result from the interaction of two or more relatively stable molecules, while in other cases one radical by reaction with a normal molecule may form a different radical.

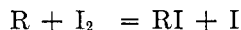
(1) *Diffusion flames*: Horn, Polanyi, and Style (129, 130, 215) modified the diffusion-flame technique so as to investigate certain reactions of free radicals. A further jet was added to the apparatus, and the products of a reaction of the type



were introduced into chlorine or iodine. In this way they were able to demonstrate the occurrence of the reactions

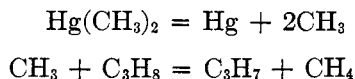


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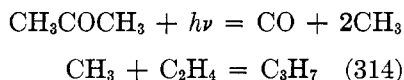


Allen and Bawn (2) have combined the method of Horn, Polanyi, and Style with the Paneth technique for the detection of radicals.

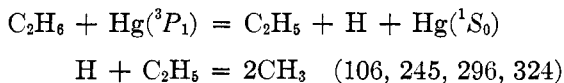
(2) *The indirect production of atoms and radicals:* Frequently the production of an atom or radical in a system leads, by reaction involving other substances, to the formation of other, different, atoms or radicals. For example, if mercury dimethyl is decomposed in the presence of propane (278), we have



Hence this method could, in principle, be used as a source of propyl radicals. Other examples are



and



However, the systems thus formed are so complex that this is rarely a satisfactory method of generating atoms or radicals. Only when the complete mechanism of the reaction can be accurately established can this method be used.

(3) *Explosions, oxidation reactions, etc.:* There is considerable evidence that atoms and radicals play a decisive rôle in many explosions, oxidation reactions, etc. (134, 163, 180). The systems are so complex, and our knowledge of them is so slight, however, that they cannot be used in practice as reliable sources of atoms and radicals.

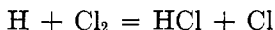
2. Photochemical

(a) Production of atoms or radicals by photolysis

A very wide variety of possibilities exist, since this section includes most of photochemistry. In many cases information about elementary reactions comes from an analysis of the mechanism of photolysis. A well-known example is the photosynthesis of hydrogen chloride, in which the primary process is the dissociation of chlorine, and the investigation of which leads to information about the secondary reactions



and

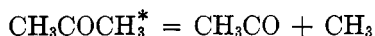


(For a recent and detailed discussion see Rollefson and Burton (254).) However, since it would obviously be out of place to enter into an extended discussion of photochemistry here, we shall consider only those cases in which a substance is deliberately photolyzed in order to provide a supply of radicals or atoms. Some of the main examples of this technique are:

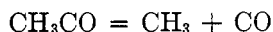
(1) *Photohalogenations*: A wide variety of photohalogenations have been investigated (for reviews see references 181a, 254, and 262a). When a halogen absorbs light in the continuum the primary process involves a split into atoms, and if some other substance is present, the atoms thus produced may react with it. In general, chain reactions occur under these circumstances. In a large number of cases detailed investigations have been made, and the mechanism of the reactions can be inferred with considerable certainty. Activation energies of the part-reactions can then be deduced by a comparison of the rate equation predicted by the mechanism with that obtained experimentally. In this way activation energies have been arrived at for a large number of reactions involving atomic chlorine and bromine, and for a few reactions involving atomic iodine. Some examples follow:



(2) *Photolysis of ketones*: The aliphatic ketones show a first absorption maximum in the neighbourhood of 2800 Å., which is associated with the carbonyl group. Much work has been done on the photolysis of a wide variety of ketones (see especially references 53, 105, 179, 181, 181a, and 279). It seems to be established that in the case of acetone the primary process is, at least to a large extent,



At higher temperatures (above 60°C.) the acetyl radical decomposes.

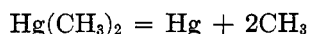


Hence at higher temperatures acetone acts as a source of methyl radicals only.

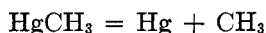
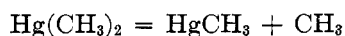
Pearson and his coworkers (100, 206, 208, 209, 210) have used mirror methods to detect and estimate free radicals in the case of acetone and numerous other ketones, and have used such photolyses as a source of free radicals. Estimates of the per cent of the primary step which involves decomposition into free radicals of various ketones are given in table 5.

Acetone has been used as a source of free radicals in the investigation of induced reactions by Leermakers (156), Taylor and Jungers (314), Maess (167), Akeroyd and Norrish (1), and Danby and Hinshelwood (53a).

(3) *Photolysis of metal alkyls*: The thermal decomposition of metal alkyls as a source of free radicals has already been discussed. The mechanism of their photolysis appears to be similar to that of their pyrolysis, yielding free alkyl radicals (52, 157, 165, 174, 181a, 220, 278, 318, 319, 320, 322). This may occur in stages; i.e., instead of

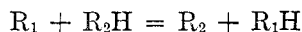


we may have



For a summary of work on the photolysis of metal alkyls see page 241.

The mercury alkyls have been much used as a source of free radicals by Taylor and his collaborators (52, 174, 278, 318), who by their use have investigated a whole series of reactions of the type



Thus, Smith and Taylor (278, 318) photolyzed mercury dimethyl in the presence of deuterium, ethane, neopentane, butane, isobutane, benzene, toluene, diphenyl-

TABLE 5

Estimates of the per cent decomposition into free radicals in the photolysis of several ketones (taken from reference 254)

KETONE	PER CENT DECOMPOSITION INTO FREE RADICALS	
	Glazebrook and Pearson	Norrish
Acetone.....	100	100
Methyl ethyl ketone.....	81	70-80
Methyl propyl ketone.....	62	
Methyl butyl ketone.....	28	10
Dipropyl ketone.....	37	37
Diisopropyl ketone.....	41	44

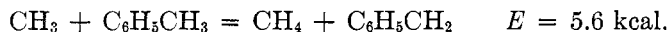
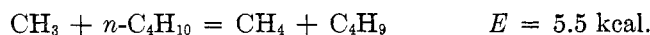
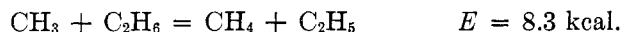
methane, and propylene. They assume in the case of the hydrocarbons that the main steps in the mechanism are as follows:



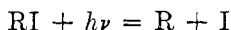
This yields for the rate of methane production

$$\begin{aligned} \frac{d}{dt}(\text{CH}_4) &= k_1(\text{RH}) \cdot \frac{-2k_1(\text{RH}) + (4k_1(\text{RH})^2 + 8k_3 I_{\text{abs.}})^{1/2}}{2k_3} \\ &= k_1(\text{RH}) \cdot A \end{aligned}$$

At low temperatures where ethane (from reaction 3) is the principal product, A will be approximately constant; hence the rate of production of methane will give a true measure of k_1 . By measuring the rate of formation of methane as a function of temperature, the activation energy of reaction 1 can therefore be obtained. In this way they found, for example,



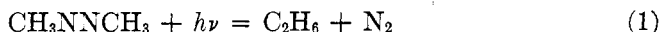
(4) *Photolysis of alkyl halides:* A great deal of work has been done on the absorption spectra and photolysis of the alkyl halides, especially the iodides (see, particularly, references 56, 62, 63, 64, 65, 181a, 329, 330, 331, and 332). There is some disagreement regarding the mechanism of the reactions, but the evidence is strongly in favor of a primary split into a radical and a halogen atom; e.g.,



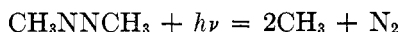
The quantum yield is low, owing to the high efficiency of the reverse reaction, but it may be increased by the addition to the system of any substance capable of fixing the iodine formed (133).

The photolysis of alkyl iodides has been used as a source of free radicals by Jungers and Yeddnapalli (137), using methyl, ethyl, propyl, and isopropyl iodides; by Tassel (306), using ethyl iodide; and by Joris and Jungers (133), using ethyl iodide.

(5) *Photolysis of azomethane:* A number of investigations of the photolysis of azomethane have been made (42, 43, 54, 82, 224, 225, etc.). Early work seemed to suggest a simple mechanism leading directly to the final products,



However, it now appears to be established that the primary step is a split into free radicals



or



and that reaction 1 does not occur to any appreciable extent.

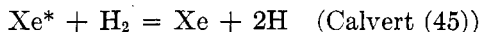
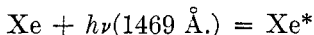
The photolysis of azomethane has been used as a source of free radicals by Maess (167) and by Blacet and Taurog (26a).

(B) PRODUCTION OF ATOMS OR RADICALS BY PHOTSENSITIZATION

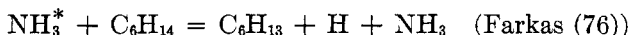
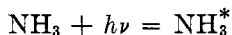
In order that a photochemical reaction may occur it is necessary (a) that the magnitude of the quantum of the incident light be large enough, and (b) that the light be absorbed. In many cases substances have dissociation energies corresponding to wave lengths in a convenient region of the spectrum, but are transparent down to the Schumann region where photochemical experiments are difficult to carry out. Thus, hydrogen has a dissociation energy of 102.7 kcal., corresponding to a wave length of 2776 \AA ., but the continuum in its absorption spectrum does not begin till 849 \AA .

If we add to hydrogen a substance which will absorb somewhere below 2776 \AA . and can transfer this energy to the hydrogen, we can produce a *photosensitized*

dissociation of hydrogen. This method is of wide applicability and a variety of sensitizers have been used for many reactions; e.g.,

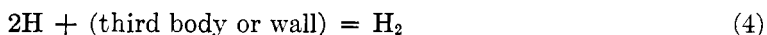
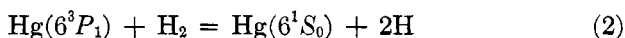
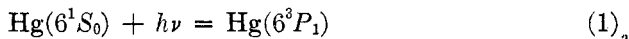


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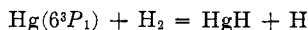
From an experimental point of view, however, the main sensitizers are metal atoms, since with them it is possible to use very intense and convenient sources of resonance radiation. Of these, mercury has been most used. In experiments of this sort mercury vapor is mixed with the reactant gas, and the mixture is illuminated with the mercury resonance line at 2537 Å. (A little work has also been done with the lower resonance line, 1849 Å. (48, 81a).) This is absorbed by the mercury vapor in the system, normal 6^1S_0 mercury atoms being raised to the 6^3P_1 level. This lies 4.8 volts, or 112 kcal., above the ground state. Such excited mercury atoms may then transfer their energy by collision to other molecules. If such transfer occurs efficiently a wide variety of reactions is possible, since 112 kcal. is greater than the activation energy of almost all chemical reactions (see, e.g., references 46, 309, 310, 311, and 316).

The mercury-photosensitization method is especially important, since Taylor and his coworkers have shown that it allows the investigation of reactions involving hydrogen atoms. In the presence of hydrogen and a reacting substance, X, we have

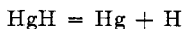


Under these circumstances a stationary concentration of hydrogen atoms exists, and, if the rates of reactions 1, 2, and 4 are known, the rate constant of reaction 3 can be calculated (see, for example, references 4, 5, 6, 7, 78, 277, 301 and 302). This is an extremely useful method, although the results are not always easy to interpret, since in many cases the reactant also "quenches" the resonance radiation to an appreciable extent, and decomposition reactions, and so on, are thus superimposed on the hydrogen-atom reaction. Examples

³ From recent work there is some doubt as to whether reaction 2 proceeds as written, or goes by the following reaction (23, 89, 187, 250)



followed by

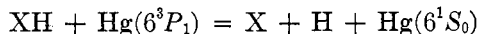


However, this would not affect the general conclusions to be drawn from experiments on photosensitization by mercury.

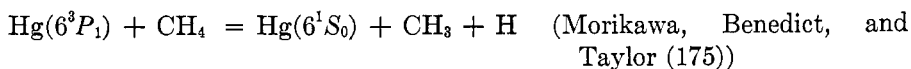
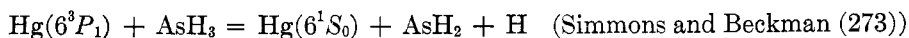
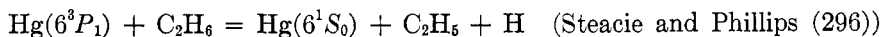
of the use of this method to investigate hydrogen-atom reactions are given below:

REACTION	INVESTIGATORS
H + CH ₄	Taylor, Morikawa, and Benedict (175, 317) Steacie and Phillips (293) Farkas and Melville (75)
H + C ₂ H ₆	Taylor and Hill (310, 311) Kemula, Mrazek, and Tolloczko (138) Steacie and Phillips (296)
H + C ₃ H ₈	Taylor and Hill (310, 311) Steacie and Dewar (286)
H + C ₂ H ₄	Taylor and Marshall (316) Taylor and Hill (310, 311) Melville (173) Jungers and Taylor (136)

By mercury photosensitization it is also possible to produce atoms and radicals by decomposition reactions, especially by reactions of the type



This has been much used, although it is generally difficult to make a sufficiently detailed interpretation of the mechanism to enable reliable estimates to be made of the activation energies of the individual elementary reactions. Examples are:

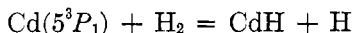


The method can obviously be used equally well for deuterium atoms (see references 75, 175, 285, and 293).

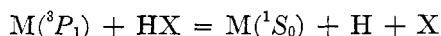
By using other metals as sensitizers it is possible to vary the energy input to the reacting molecule. Thus, with mercury, cadmium, and zinc the following excitation energies are involved:

SENSITIZER	EXCITATION ENERGY
	<i>kcal.</i>
Hg(6 ¹ P ₁) (1849 Å.)	153.9
Hg(6 ³ P ₁) (2537 Å.)	112.2
Cd(5 ¹ P ₁) (2288 Å.)	124.4
Cd(5 ³ P ₁) (3261 Å.)	87.3
Zn(4 ¹ P ₁) (2139 Å.)	133.4
Zn(4 ³ P ₁) (3076 Å.)	92.5

In the case of cadmium (and probably zinc), however, there is one important difference. Olsen's work (187) makes it probable that with mercury-hydrogen mixtures the primary step is a direct split into two hydrogen atoms, rather than an intermediate formation of mercury hydride. However, in the case of cadmium-hydrogen mixtures illuminated with the resonance line at 3261 Å., Bender (19) and Olsen have obtained strong resonance excitation of CdH bands. This indicates that CdH is formed in the normal state, and suggests that the primary step is



It is, therefore, not at all certain *a priori* whether with reactions involving a C—H bond split in a hydrocarbon or other organic molecule, we have in a given case



or



If the latter mechanism holds, the bond split will be less endothermic by an amount equal to the heat of formation of the hydride. Hence bonds may be broken which are "stronger" than the excitation energy of the metal atom by 8.5 kcal. in the case of mercury, 15.5 kcal. in the case of cadmium, and 23.1 kcal. in the case of zinc. There is no doubt that some cadmium-photosensitized reactions proceed in this way.

A number of investigations of reactions photosensitized by cadmium and zinc have recently been made (283). Some examples are given below:

REACTION	INVESTIGATORS
$\text{Cd}(5^3P_1) + \text{C}_2\text{H}_6$	Steacie and Potvin (297)
$\text{Cd}(5^3P_1) + \text{C}_2\text{H}_8$	Steacie, LeRoy, and Potvin (290)
$\text{Cd}(5^3P_1) + \text{C}_2\text{H}_4$	Bates and Taylor (15)
$\text{Cd}(5^3P_1) + \text{C}_2\text{H}_4$	Steacie and Potvin (298)
$\text{Cd}(5^1P_1) + \text{C}_2\text{H}_4$	Steacie and LeRoy (289)
$\text{Zn}(4^3P_1) + \text{C}_2\text{H}_4$	Steacie, Habeeb, and Le Roy (288)
$\text{Zn}(4^1P_1) + \text{C}_2\text{H}_4$	Steacie, Habeeb, and Le Roy (288)

An investigation of sodium photosensitization, using the D-doublet, has also been made by Jungers and Taylor (135). They found that ethylene quenched the radiation but was not chemically affected. The reason is, apparently, that the energy associated with this line (48 kcal.) is too small to cause decomposition or polymerization of ethylene.

3. Electrical

(a) Production of the active species by an electrical discharge

(1) *The reactant is itself in the discharge:* (For comprehensive recent reviews of the theory and chemical action of electrical discharges see references 101 and 321.)

There are two fundamentally different types of electrical discharge, the silent or non-disruptive discharge, and the disruptive discharge.

The silent discharge includes a number of types, such as the ozonizer, semi-corona, corona, glow, and electrodeless discharge. These have been used in numerous investigations with a variety of substances. There is no doubt that in many cases atoms and radicals are formed by the decomposition of organic or inorganic compounds. However, the situation is usually too complex to permit any accurate conclusions as to the rates of elementary reactions. On the other hand, the results are sometimes of value as confirmatory evidence for postulated mechanisms.

The disruptive discharges, the arc and the spark, are much more violent in nature. There is no doubt that the main effects of these discharges are thermal, and correspond to localized heating of the gas to 1500°C. or higher. In general, the results produced are so drastic that almost every possible atom or radical is produced by the discharge, and it is impossible to obtain much information about specific chemical reactions from work of this kind.

(2) *The products from a discharge are mixed with another substance: Hydrogen atoms*—As we have seen, atoms and radicals are produced in electrical discharges in gases. It was first shown by Wood (336, 337, 338, 339) that hydrogen atoms could be pumped out of a glow discharge in hydrogen and carried for considerable distances before they recombined. He found that for the success of the experiment it was essential that the walls of the tube be "poisoned" to slow down the recombination of the atoms, and that this could be done by a trace of water.

Following preliminary experiments by Taylor and Marshall (315a), Bonhoeffer (28, 29, 30, 31) modified Wood's apparatus and made extensive investigations of the chemical properties of atomic hydrogen. A typical apparatus for this kind of investigation is shown in figure 3. Hydrogen flows through a discharge tube carrying about 300 milliamperes at several thousand volts. By the use of a fast pump and large connecting tubing the rate of flow through the apparatus is made very high, about 3 meters per second; hence atoms are drawn out of the tube into the reaction vessel before much recombination has occurred. The other reactant is added through a jet leading into the reaction vessel. As in Wood's work, it is essential that the walls of the vessel be thoroughly poisoned to prevent catalytic recombination of the atoms. This can be done with water vapor, as used by Wood (for a modification see Trenner, Morikawa, and Taylor (324)), syrupy phosphoric acid (328), fused solid phosphoric acid (217), or potassium chloride (98). With efficient poisoning 20 to 50 per cent of hydrogen atoms may readily be obtained in the reaction vessel. The methods by which the hydrogen-atom concentration may be measured are described in a later section.

The pressures used are usually in the range 0.2 to 0.5 mm. With the pumping speeds employed, this is generally equivalent to a contact time of 0.5 to 1 sec. Under these conditions the rates of reactions involving hydrogen atoms can be

measured at room temperature, provided the activation energies are in the range 5 to 12 kcal.

The method has been used by a number of investigators at temperatures up to 180°C., and by Steacie up to 500°C. (282). At such high temperatures wall

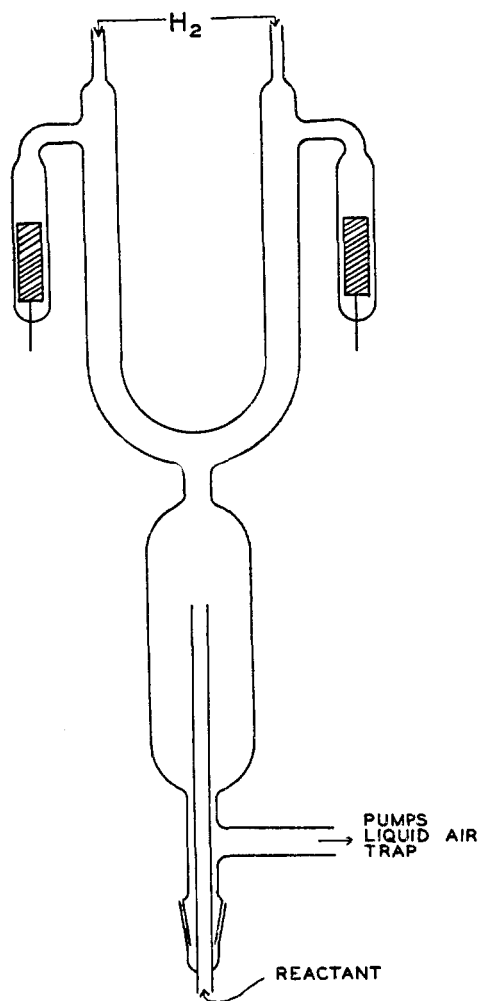


FIG. 3. Discharge-tube method for investigating the reactions of hydrogen atoms

poisoning becomes difficult, and only relatively low hydrogen-atom concentrations can be obtained (*ca.* 1 per cent). Reactions at liquid-air temperatures have been investigated by Geib and Harteck (95, 96).

The method has been modified by Harteck and Roeder (115, 116, 117). By adding an inert gas such as neon as a carrier, it was possible to operate the discharge at pressures up to 20 mm. The issuing mixture of hydrogen molecules,

hydrogen atoms, and neon could then be bubbled through liquids and the reactions of atomic hydrogen with dissolved substances investigated. (See, however, Klemenc (141) for a criticism of this method.)

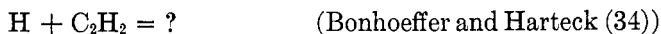
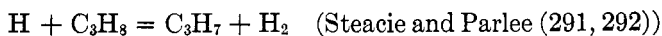
In only a few investigations by the Wood-Bonhoeffer method have activation energies been determined from the temperature coefficient of the reaction in the ordinary way. The reason for this is that measurements of atom concentration are not very accurate, and since the reactions investigated have low temperature coefficients, these temperature coefficients cannot be accurately determined. In most cases, therefore, the investigations have been carried out at room temperature only. The results are then expressed in the form of a collision yield, calculated as the fraction of the number of collisions of a hydrogen atom with the reactant which are effective in causing reaction. The activation energy of the reaction is then usually estimated from the relation

$$x = Ze^{-E/RT}$$

where x is the collision yield, and Z is a steric factor, which is usually assumed to be equal to 0.1. This assumption is arbitrary, but is probably not far wrong in most cases, and the activation energies estimated in this way are thus usually reliable. If, however, a reaction happened to have a very small steric factor, say 10^{-4} , the activation energy estimated from the collision yield on the assumption that $Z = 0.1$ would be entirely misleading.

Surface effects probably constitute the main source of error in this method. It is practically impossible to estimate what fraction of the observed reaction may occur catalytically on the walls of the reaction vessel (75, 98).

A very large number of hydrogen-atom reactions have been investigated in this way (for a review see Geib (91)). Examples are the following:



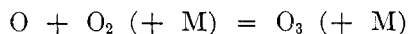
(v. Wartenberg and Schultze (327))

The method has been applied to deuterium-atom reactions by a number of workers (98, 107, 324); the results have been reviewed by Geib (92).

It is obvious that it would be possible to produce hydrogen atoms at higher pressures by means of a streaming method with an arc or spark discharge. However, under such circumstances the rate of flow would necessarily be relatively slow, the higher pressure would aid recombination of the atoms, and thus only minute quantities of atoms could be withdrawn from the tube. A very large number of claims of "active" modifications of hydrogen produced in this way have been made, but the results in all cases appear to be due to traces of impurity in the hydrogen.

Oxygen atoms—Wood's method has also been applied to oxygen by a number of investigators (10, 11, 24, 49, 253, 341). The main knowledge of oxygen-atom

reactions by this method comes from the work of Harteck and Kopsch (112, 113, 114) and of Geib (91), who used apparatus identical with that described above for hydrogen atoms. One complicating factor in dealing with oxygen-atom reactions is the formation of ozone by the reaction



At low pressures and at temperatures from room temperature upward, however, this is relatively unimportant and the only "active" modification of oxygen present is atomic oxygen. Low-temperature investigations of oxygen-atom reactions have been made by Geib and Harteck (96, 97) and by Schenk and Jablonowski (259, 259a). Nalbandyan (177, 178) has produced oxygen atoms from a discharge and by sudden compression has obtained appreciable atom concentrations at relatively high pressures.

The hydroxyl radical—The presence of the hydroxyl radical can be demonstrated spectrographically in emission in the gas flowing from a Wood's tube with moist hydrogen (29), moist oxygen, or water vapor (153). Oldenberg (185) has succeeded in photographing the hydroxyl bands in absorption under similar conditions. However, the situation produced is highly complex, since we may have present also H, O, H₂O₂, HO₂, etc. As a result it is difficult to interpret the results obtained (87, 88, 113, 184, 185, 186, 304, 325, 333).

Nitrogen atoms—These can also be obtained by Wood's method (112, 340, 341, 259a).

Chlorine atoms—Rodebush and Klingelhoeffer (252) produced atomic chlorine by means of a high-frequency discharge. A flow system with a fast pump was used, and atomic chlorine could be pumped out of the tube for some distance. In this way concentrations of atomic chlorine up to about 20 per cent, as measured with a Wrede gauge, were obtained.

Schwab and Friess (265, 266, 267) have prepared atomic chlorine in concentrations up to 40 per cent by Wood's method. The atom concentration was measured calorimetrically. The main difficulty is to prevent too rapid recombination of the atoms on the material of the electrodes. They found that water-cooled iron electrodes gave the best results. On account of the very rapid recombination of the atoms on the walls of the apparatus (one collision in about twenty is effective), the results obtained are much more difficult to interpret than is the case with hydrogen atoms.

Bromine atoms—Schwab (264) investigated atomic bromine by Wood's method. It was found by calorimetric means that practically every collision of a bromine atom with the wall led to recombination, irrespective of the wall material. As a result, it was not possible to investigate reactions of atomic bromine with other substances.

Free radicals—Rice and Whaley (248) used Wood's method with a variety of organic compounds, *viz.*, butane, pentane, ethylene, methanol, ethyl alcohol, acetaldehyde, acetic acid, and acetone. The products were passed over metallic mirrors in an attempt to identify the radicals produced. They found that the fragments removed antimony and lead mirrors, but not zinc or cadmium.

Hydrogen atoms were undoubtedly present, but the evidence points to radicals as well, although these were not definitely identified. The work would well merit extension.

(b) Production of the active species by collision with ions

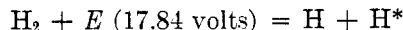
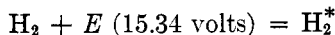
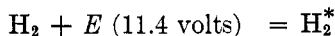
The ions may be produced (a) by radioactive sources (164) or (b) by fast electrons (101). Many reactions occur under these influences, and the results obtained are of definite interest by comparison with photochemical and thermal reactions of the same substances. As yet, however, no information leading directly to the rates of elementary processes has been obtained in this way.

(c) Production of the active species by collision with slow electrons (of controlled speed)

It is obvious that if an electron with an energy of, say, 7 or 8 volts collides with a molecule and transfers its energy to it, reaction can occur. In principle it should be possible to investigate many interesting reactions by using electrons of controlled speed (101). Actually, however, it is found that energy transfers of this sort are not effective by mere "collision," but only occur when the molecule is raised to an excited state which may then dissociate. Thus with hydrogen the possible process

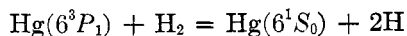
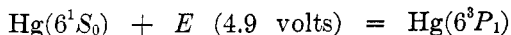


does not occur. Hydrogen, however, can be dissociated or excited by such processes as the following:



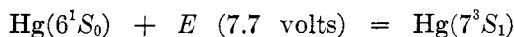
Such methods open up interesting possibilities in the investigation of the reactions of excited atoms and molecules. However, as yet no detailed information on ordinary elementary processes has been obtained from such work.

An interesting modification of the method is the investigation of mercury-sensitized processes by Glockler and Thomas (102). It was found that dissociation of hydrogen did not occur in the presence of mercury vapor and electrons of 4.9 volts energy, although it might have been expected by the mechanism

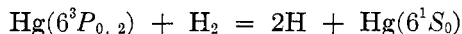


However, the hydrogen pressure used was very low (*ca.* 10^{-2} mm.), and almost all excited mercury atoms would radiate rather than be quenched by hydrogen.

With electrons of 7.7 volts energy dissociation of hydrogen occurred, presumably by the formation of metastable atoms by the following reactions



The metastable mercury atoms thus formed are then quenched by hydrogen to an appreciable extent on account of their relatively long life; i.e.,



B. THE DETECTION AND ESTIMATION OF ATOMS AND RADICALS

The methods of detection and estimation of atoms and radicals may be classified as follows: (1) by chemical properties, (2) by spin-isomerization, isotopic labelling, etc., (3) by physical properties, (4) by optical methods, and (5) by inference.

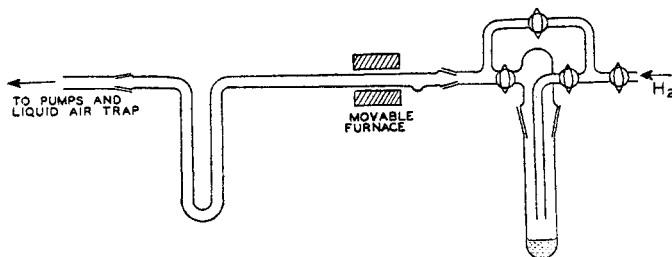


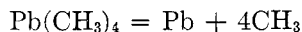
FIG. 4. The Paneth method of detecting free radicals

1. Chemical properties

(a) The removal of mirrors

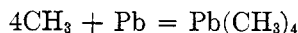
It was first shown by Paneth and Hofeditz (192) that free methyl radicals could be detected by their reaction with a metallic mirror deposited on the walls of a tube through which a carrier gas together with the radicals was flowing.

The apparatus is shown in figure 4. A stream of hydrogen which had been specially purified was passed at a low pressure, of the order of 1 to 2 mm., through a cooled vessel in which it was saturated with lead tetramethyl vapor, and was then led through a hard-glass tube. One end of this tube was heated with a Bunsen burner, or better, with an electric furnace (194), and in this the flowing lead tetramethyl was decomposed. The decomposition proceeded presumably by the reaction

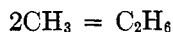


and a "mirror" of lead was deposited on the walls of the tube. If now the tube was heated "up-stream" from the lead mirror, it was found that the first mirror gradually disappeared, even if the distance was as great as 30 cm., although the rate of removal was slower the greater the distance. This is strong evidence

that the methyl radicals produced in the decomposition were removing the lead mirror by the reaction



The success or failure of the method depends entirely on the speed of the pumping system, since it is essential to carry the methyl radicals along the tube for considerable distances before they disappear by the reaction



or other reactions. In Paneth and Hofeditz' work a fast diffusion pump was employed, which with a pressure of 1–2 mm. in the apparatus produced linear speeds through the tube up to 16 meters per second. At such speeds no diffusion against the flow occurred, and free lead was never deposited ahead of the heated zone.

Tests were made to prove that the phenomenon of mirror removal was not due to thermal effects produced by the stream of hot hydrogen. In the first place a flame very close to a lead mirror caused no effect when a stream of pure hydrogen (without lead tetramethyl) was used, other than a very slow creeping forward of the edge of the mirror. Secondly, water cooling of the tubing between the heated zone and the mirror did not prevent the removal of the mirror. (Direct cooling of the mirror itself by water often inhibited mirror removal, owing to the deposition on the mirror of traces of high-boiling substances.)

Tests showed that some lead tetramethyl passed the burner without decomposition, and in later work an electrically heated spiral of wire was wound round the tube just past the flame. Under these circumstances complete decomposition occurred.

Antimony and zinc mirrors were also used successfully.

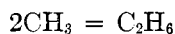
Experiments were made by Paneth and Hofeditz to determine the lifetime of the free methyl radical. Antimony mirrors were deposited on the walls of the tube under controlled conditions, so that the same amount of metal was deposited in each case. (The experimental methods of obtaining such standard mirrors are not given in any further detail by Paneth and Hofeditz.) The mirrors in successive experiments were placed at different distances from the heated zone, and the time required for the removal of the mirrors was measured. In this way it was possible to follow the decrease in the concentration of methyl radicals as the distance from the heated zone was increased. In these experiments a streaming velocity of 14 meters per second was used, and the lead tetramethyl concentration in the stream corresponded to its vapor pressure at -70°C . The total pressure was approximately 2 mm. The results are given in table 6.

When $\log A$ is plotted against the distance, l , or the time, z , a straight line is obtained. In other words, the concentration of radicals, or activity, falls off with time according to a first-order law. This is illustrated by the data in table 7, in which the later values only are used, since the values with the mirror very close to the heated zone are not so reliable. In the table t is the time taken

by the radicals in travelling from $l = 13$ cm. to $l = l$, A_1 is the activity at $l = 13$ cm., and A_2 is that at $l = l$. Whence we obtain

$$\text{Half-life} = 1/k_{\text{unimolecular}} = 5.8 \times 10^{-3} \text{ sec.}$$

The unimolecular nature of the "decay" is surprising, since it might be expected that the radicals would disappear by the reaction



There are two obvious possible explanations: (a) The reaction

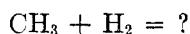


TABLE 6

DISTANCE, l , FROM HEATED ZONE TO MIRROR	TIME, z , TAKEN TO TRAVEL THIS DISTANCE	TIME, d , REQUIRED TO REMOVE THE MIRROR	ACTIVITY, A $A = \frac{1}{1000d}$	$\log_{10} A$
cm.	seconds	seconds		
4	2.9×10^{-3}	4	250.0	2.40
8	5.7	11	90.9	1.96
13	9.3	20	50.0	1.70
18	12.9	25	40.0	1.60
22	15.7	45	22.2	1.35
28	20.0	70	14.3	1.16
33	23.6	100	10.0	1.00
37	26.4	150	6.7	0.82

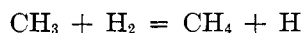
TABLE 7

Data illustrating the first-order loss of activity

l	z	t	A	$\log_{10} A_1/A_2$	$k = 1/t \ln_e A_1/A_2$
cm.	seconds	seconds			
13	9.3×10^{-3}	0	50.0		
22	15.7	6.4×10^{-3}	24.2	0.35	127
28	20.0	10.7	14.3	0.54	117
33	23.6	14.3	10.0	0.70	113
37	26.4	17.1	6.7	0.88	118

i.e., the methyl radicals disappear by reaction with hydrogen. This is in large excess, and hence the loss of radicals will follow a first-order law. (b) The radicals disappear by a first-order wall reaction. The obvious method of deciding between these is to use other carrier gases.

In a further paper Paneth and Lautsch (195) investigated the lives of the methyl and ethyl radicals when hydrogen and helium-neon mixtures were used as carrier gases. The lives found were not very different in the two cases and they therefore drew the following conclusions: (a) Radicals do not disappear in hydrogen to an appreciable extent by the reaction



(b) At the pressures concerned three-body collisions are rare, and the recombination process



cannot be important. (c) Hence radicals disappear mainly at the wall. However, calculations show that by no means all collisions with the wall are effective in producing recombination (actually, only about one collision in one thousand is effective).

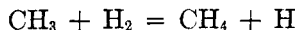
By using a "guard mirror" before the regular mirror and increasing its width in successive experiments, they found the maximum width of mirror necessary to remove all the radicals. These results indicate (191) that every collision of a radical with the mirror results in the formation of metalloorganic compounds.

Paneth and Lautsch also found that if a portion of the tube was cooled to -180°C . all radicals were removed. Hence, even with glass, the accommodation coefficient is approximately unity at very low temperatures. At higher temperatures the life increases, presumably because the accommodation coefficient decreases, up to about 500°C . At still higher temperatures the life decreases again. In helium at 500°C . the life of the methyl radical can be raised to 0.1 sec. (193).

Paneth and Lautsch also showed that iron and platinum had no catalytic effect on the recombination (see also Paneth (188)). Since iron removes atomic hydrogen, this proves that the effects found by Paneth and his coworkers with mirrors are not due to hydrogen atoms, as claimed by Schultze and Müller (260). They also found (194) that lead, arsenic, antimony, zinc, and cadmium mirrors were effective.

Precautions in the control of flow rates, etc., have been described by Paneth Hofeditz, and Wunsch (193).

Later work (193) seems to indicate that the wall effect was overestimated by Paneth and Lautsch, and that even at room temperature a fair amount of methyl disappears by the reaction



One further significant fact emerges from the work of Paneth, Hofeditz, and Wunsch. Lead tetramethyl was decomposed in the apparatus in the usual way. This deposited a lead mirror, which we may distinguish as mirror I. The alkyl radicals formed in the decomposition of the lead tetramethyl which resulted at the time of formation of mirror I reacted with a second mirror and formed lead tetramethyl again. This was decomposed again, and a new mirror, II, was formed. The amount of lead in mirror I was then compared with that in mirror II. The result found was that at low lead tetramethyl concentrations up to 82 per cent of the lead at mirror I was found at mirror II. Hence the yield of free methyl radicals on decomposing lead tetramethyl by the Paneth technique is almost 100 per cent.

Rice, Johnston, and Evering (238, 242) greatly simplified the experimental arrangement by substituting condensable gases for hydrogen or helium as

carriers. Using water vapor, carbon dioxide, or organic solvents as carriers, it is possible to freeze the carrier out with liquid air. Under these circumstances high-speed pumps are unnecessary. The simplified apparatus is shown in figure 5.

"A 1% solution of lead tetramethyl in acetone or heptane is put into tube A. The stopcock 1 is opened and the apparatus is evacuated. This automatically removes all oxygen from the apparatus and after one or two minutes the stopcock is again closed. The furnace is then heated to 500-600° and a metallic mirror is formed by heating a piece of metal which has previously been introduced into the quartz tube at C. The mirror is cooled with water, the stopcock 1 is opened, and the current of gas containing the free methyl groups is allowed to pass over the mirror."

"Numerous classes of organic compounds, such as hydrocarbons, ketones, ethers, etc., can be decomposed into free radicals in the apparatus shown in Fig. 2 (figure 5 in this paper). The vapor of the material itself is used as transport gas for the free radicals; the only modification in method, from that used when an organo-metallic compound is decomposed, is that the furnace must be heated to a higher temperature, usually in the range 750-950°C.

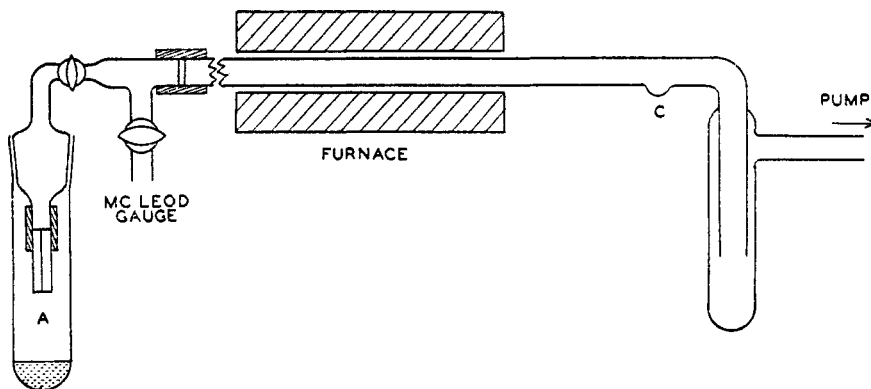


FIG. 5. The Rice apparatus for investigating free radicals

When using this apparatus for the decomposition of non-metallic compounds, the flask A containing the compound is evacuated for a few minutes so as to remove all air from the apparatus. The temperature of the flask and the size of the capillary are so adjusted that the vapor pressure at the inlet end of the quartz tube B is in the range 0.5 to 2 mm. A good oil pump, capable of producing a vacuum of 0.05 mm., is sufficient, although an auxiliary mercury vapor pump is desirable on account of the higher speed of evacuation."

Rice and his collaborators have shown (242) that a wide variety of metals may be used as mirrors: viz., lithium, sodium, potassium, calcium, zinc, cadmium, mercury, lanthanum, thallium, tin, lead, arsenic, antimony, bismuth, selenium, and tellurium. Negative results were obtained with magnesium, copper, silver, gold, and cerium.

In connection with the Paneth-Rice method, it should be noted that it is merely the standard flow method, except that the speed of flow is unusually high. The distinctive features of the work are the methods of detection of the radicals. As we shall see, the main difficulties associated with the application of the method to the determination of the activation energies of elementary reactions arise in

connection with the methods of detection, which are a matter of very great experimental difficulty.

Paneth and Hofeditz found that the mirrors often lost their activity if the tube was cooled by running water, owing to the deposition on the mirror of traces of high-boiling substances which prevented the access of radicals to the mirror. Mirrors may also be formed, and more conveniently, by introducing a small pellet of metal into a small depression in the tube, and heating the tube at this point with a current of gas flowing through it. Some of the metal is thus volatilized and deposited "down-stream" as a mirror on the colder parts of the apparatus.

It is essential that all air be excluded from the apparatus, since a trace of oxygen will deactivate the mirror, presumably by forming an oxide layer on the surface.

In using "standard mirrors" Paneth and Lautsch (195) encountered considerable difficulty in obtaining reproducible results. It was not possible to reproduce each time the surface condition of the mirrors, even though they contained the same quantity of metal. The difficulty was less, but still considerable, in new glass or quartz tubes. In consequence they reported their results as only provisional in a quantitative sense.

Paneth and Hahnfeld (190) found that results with tellurium were much more reproducible, since tellurium mirrors are not inactivated by traces of oxygen as are mirrors of other metals. They determined the activity not by the time for the removal of a mirror, but by its loss in weight. Details of their procedure were not given.

The use of tellurium mirrors was extensively investigated by Rice and Glasebrook (235). They also pointed out (233, 234) that in some cases mirrors are definitely specific in action. Thus methylene removes tellurium, antimony, selenium, and arsenic, but does not attack zinc, cadmium, bismuth, thallium, or lead, all of which are readily removed by alkyl radicals. The effect was shown by experiments in which the removal of mirrors was investigated, using the products of the decomposition of ether and of ether-diazomethane mixtures. The pyrolysis of ether yields methyl radicals, while that of diazomethane gives methylene. It was found that there was very little difference in the rate of removal of zinc mirrors on substituting an ether-diazomethane mixture for pure ether. However, antimony and tellurium mirrors were removed much more rapidly with the ether-diazomethane mixture. The results are illustrated by figures 6 and 7 (reproduced from Rice and Rice (242)).

Rice and his collaborators (242) also investigated the effect of the temperature of the mirror on its activity. They found that the activity of lead mirrors diminished rapidly at higher temperatures. Thus, a mirror which was removed in about 20 sec. at room temperature required over 200 sec. at 325°C. under the same conditions of radical concentration, etc. In agreement with Paneth and Hofeditz, they found that lead mirrors were frequently inactivated by cooling to 0°C., presumably owing to the deposition of traces of gummy materials on the mirror. In the case of antimony mirrors the activity remained approximately constant up to high temperatures.

Rice and Johnston (237) used the standard mirror technique to investigate the activation energy of the decomposition of organic substances into free radicals. The organic compound was passed through a furnace under conditions such that only a small fraction of it decomposed. A standard mirror was placed at a definite distance from the end of the furnace and its time of removal was noted. The furnace temperature was then varied, and the time of removal of similar mirrors was determined as a function of the furnace temperature.

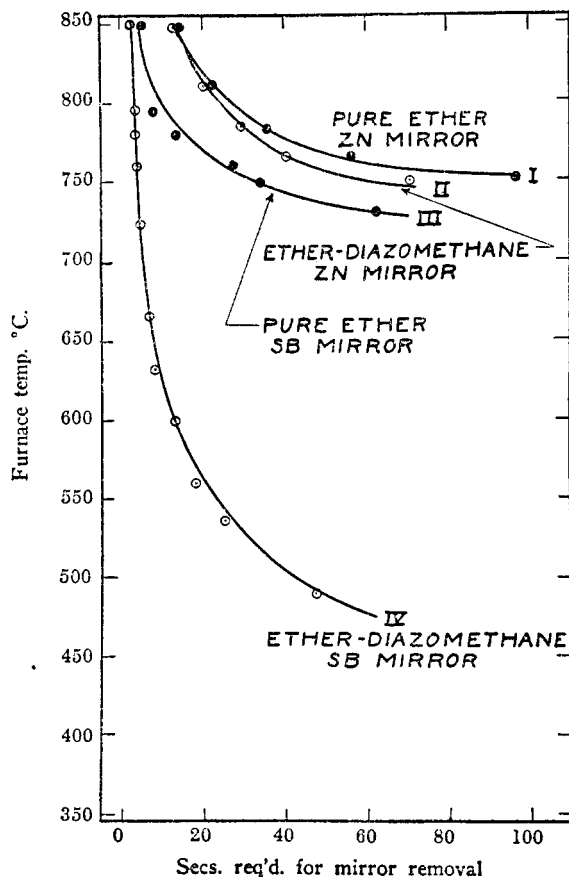


FIG. 6. The removal of zinc and antimony mirrors by methyl and methylene radicals

Since the removal time of the mirror is a measure of the radical concentration, and since this concentration is for small fractional decompositions a measure of the rate constant of the decomposition, we can thus determine the temperature coefficient of the split into free radicals, and the activation energy.

Glazebrook and Pearson (100, 207) found that mirrors, including those of tellurium, were deactivated by traces of oxygen. They also found that the activity diminished on standing, owing perhaps to the gradual evolution of oxygen from the walls of the apparatus, or to crystallization of the metal. In

depositing standard mirrors Pearson used a smoked-glass tube as a comparison standard and measured the opacity (206, 209).

Prileshajeva and Terenin (220) adapted the Paneth technique by determining the rate of disappearance of the mirror by measuring its opacity photometrically. They found an induction period in the mirror removal, probably owing to the necessity of removing adsorbed gas before the mirror itself could be attacked.

In order to make the Paneth test more sensitive, Leighton and Mortensen

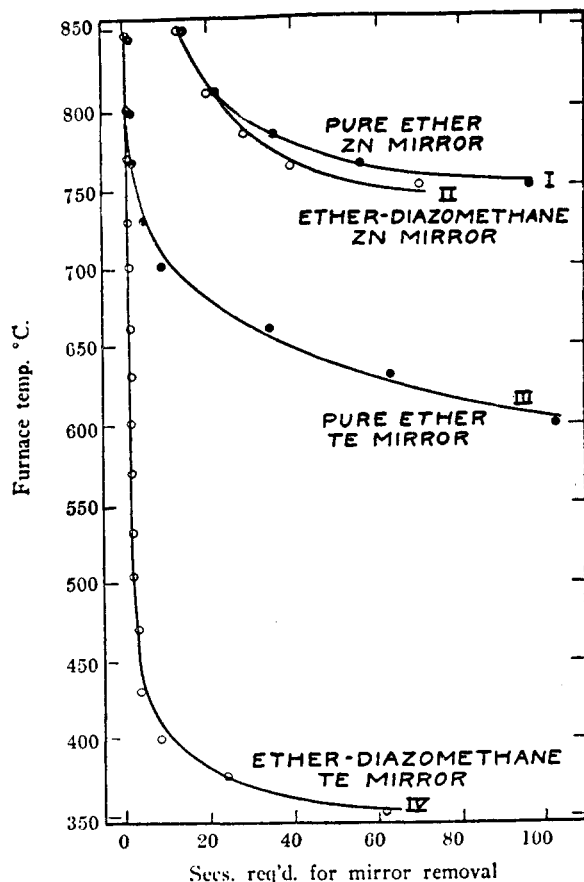


FIG. 7. The removal of zinc and tellurium mirrors by methyl and methylene radicals

(157) used lead containing radium D, radium E, and radium F (from old emanation tubes). A beta-ray electroscope was placed above the "mirror," which was so thin as to be invisible, and the disappearance of the mirror was followed by the loss of beta-ray activity. A liquid-air trap was placed in the line following the reaction tube, and its contents were also examined for beta-ray activity. They thus succeeded in detecting methyl radicals from the photolysis of lead tetramethyl. It was observed that only radium D (a lead isotope) was carried over, while radium E (a bismuth isotope) was not.

The radioactive-indicator method was also employed with modifications by Burton, Ricci, and Davis (44). They used a radium D mirror, and put the gases passing the mirror through a cracking furnace at 400° to 500°C. This decomposed the lead tetramethyl formed by the attack of methyl radicals on the mirror. The lead resulting from the decomposition of the lead tetramethyl carried over was then examined for radioactivity by cutting out the section of the tube where it deposited, dissolving the lead in hot nitric acid, and evaporating the solution to dryness. The lead nitrate formed was then examined with a Lind electroscope. They announced that further work was in progress, using radioactive antimony.

TABLE 8
Substances tested as detectors for free radicals

POSITIVE RESULTS		NEGATIVE RESULTS	
Substance	References	Substance	References
Lead.....	(192, 239)	Oxides*.....	
Bismuth.....	(192, 239)	Benzoic acid.....	(195)
Lithium.....	(239)	Copper.....	(239)
Calcium.....	(239)	Gold.....	(239)
Mercury.....	(239)	Mercurous chloride.....	(239)
Arsenic.....	(239)	Magnesium.....	(239)
Iodine.....	(16, 17, 18)	Silver.....	(239)
Antimony.....	(192, 239)	Cerium.....	(239)
Sulfur.....	(192)	Mercurous bromide.....	(239)
Sodium.....	(239, 274)	Lead chloride.....	(239)
Tin.....	(239)	SnI ₃	(239)
Lanthanum.....	(239)	Eosin.....	(239)
Selenium.....	(239)	Lead iodide.....	(239)
Zinc.....	(192, 239)	Indigo.....	(239)
Tellurium.....	(195, 239)		
Potassium.....	(239)		
Cadmium.....	(239)		
Thorium.....	(239)		
Carbon tetraiodide.....	(274)		

* It may be inferred that most oxides are ineffective, since mirrors are inactivated by traces of oxygen.

Pearson, Robinson, and Stoddart (212) have shown that the Paneth technique may be used to detect hydrogen atoms. They found that atomic hydrogen removed arsenic, antimony, selenium, tellurium, germanium, and tin mirrors, but did not affect lead or bismuth, except for a slow movement down the tube with bismuth due to distillation. This effect did not occur with lead. Burton (39, 40) has improved the method and has used it to detect hydrogen atoms in photolyses. A heavy lead "guard mirror" was deposited first, followed by a very light antimony mirror. The guard mirror served to remove alkyl radicals, and thus allowed only hydrogen atoms to pass. These removed the antimony mirror. The method has been used by Burton and his collaborators in a number of cases (125, 168).

A large number of rather varied substances have been tried as detectors for free radicals by the mirror technique, as shown in table 8.

Kohanenko (143) has used screens of zinc sulfide instead of mirrors to detect atoms and radicals. These screens glow when atoms or radicals recombine on them.

(b) The estimation of the products resulting from mirror removal

For reviews of this subject see references 207 and 242.

Paneth and Hofeditz (192) identified the methyl radical in their original experiments by passing the gas over zinc mirrors and characterizing the zinc dimethyl formed by its melting point, boiling point, and spontaneous combustion in air with the formation of zinc oxide. They also roughly identified the antimony alkyls formed when antimony mirrors were used. Paneth and Lautsch (194) identified the ethyl radical similarly. They also partially oxidized

TABLE 9
Products formed by the reaction of free alkyl radicals with mirrors

METAL	PRODUCTS					
Lead.....	Pb(CH ₃) ₄	Pb(C ₂ H ₅) ₄				
Arsenic.....	As(CH ₃) ₃	As(C ₂ H ₅) ₃	[As(CH ₃) ₂] ₂	[As(C ₂ H ₅) ₂] ₂	(AsCH ₃) ₅	(AsC ₂ H ₅) ₅
Antimony.....	Sb(CH ₃) ₃	Sb(C ₂ H ₅) ₃	[Sb(CH ₃) ₂] ₂	[Sb(C ₂ H ₅) ₂] ₂ *		
Bismuth.....	Bi(CH ₃) ₃	Bi(C ₂ H ₅) ₃	[Bi(CH ₃) ₂] ₂			
Selenium.....	Se(CH ₃) ₂	Se(C ₂ H ₅ CH ₂) ₂	(SeCH ₂) ₂			
Tellurium.....	Te(CH ₃) ₂	Te(C ₂ H ₅) ₂	(TeCH ₃) ₂ *	(TeCH ₂) ₂ *		
Zinc.....	Zn(CH ₃) ₂	Zn(C ₂ H ₅) ₂				
Mercury.....	Hg(CH ₃) ₂	Hg(C ₂ H ₅) ₂	Hg(C ₂ H ₅) ₂	(HgCH ₃) ₂	Hg(C ₂ H ₅) ₂	Hg(C ₂ H ₅ CH ₂) ₂
Beryllium.....	Be(CH ₃) ₂	Be(C ₂ H ₅) ₂				
Iodine.....	CH ₃ I	C ₂ H ₅ I	CH ₂ I ₂			

* Products formed only with warm mirrors.

the zinc ethyl to C₂H₅OOZnC₂H₅, hydrolyzed this, and identified the resulting ethyl alcohol by the iodoform test.

Sodium has also been used for identification purposes by Simons and Dull (274). The free radicals (methyl or ethyl) were allowed to come in contact with metallic sodium, forming a sodium alkyl. The mixture of sodium and sodium alkyl was treated with alcohol, whereupon methane was evolved in the case of methyl, or ethane in the case of ethyl.

Simons and Dull also used carbon tetraiodide as a detector. Methyl radicals formed methyl iodide, which was allowed to react with quinoline, and the resulting quinoline methiodide was identified.

The products formed when free alkyl radicals react with a variety of mirrors have been summarized by Rice (242) and by Pearson (207), and are given in table 9. The information comes from a variety of sources (16, 17, 18, 100, 189, 197, 208, 209, 210, 228, 232, 234, 238).

The main difficulty in all this work is the very small amount of product which must be identified. In identifying the radicals from hydrocarbon decompositions Rice, Johnston, and Evering (238) developed a technique which

has been widely used. The organometallic compounds formed by the interaction of radicals with metallic mirrors were caught in a liquid-air trap. It is very difficult to identify the compounds thus obtained, since they are mixed with a very large excess of other substances. The following procedure was therefore adopted: The radicals from the heated zone were brought into contact with a water-cooled surface on which mercury was continually condensing. In this way mercury alkyls were formed, and these were condensed in a liquid-air trap. The trap contained a few cubic centimeters of a saturated alcoholic solution of mercuric bromide. By this method alkylmercuric bromides were obtained in quantities up to about 1 g. After the material had been freed from excess mercury, etc., the residue was sublimed in a vacuum below 50°C. for an hour or two, and was thus separated from the less volatile excess of mercuric bromide. The alkylmercuric bromides were then separated by fractional sublimation. In this manner the results shown in table 10 were obtained from the radicals formed in the decomposition of butane. The authors were unable to obtain

TABLE 10

Alkylmercuric bromides obtained from the radicals formed in the decomposition of butane

FRACTION	TIME OF SUBLIMATION	TEMPERATURE OF SUBLIMATION	YIELD	MELTING POINT
	<i>hours</i>	°C.	<i>grams</i>	°C.
1	1.0	40	0.217	157
2	1.0	50	0.161	160.5
3	1.5	50	0.110	172
4	1.5	50	0.048	181.5
5	1.0	60	Trace	

Melting point of CH_3HgBr = 160°C., of $\text{C}_2\text{H}_5\text{HgBr}$ = 193.5°C., of HgBr_2 = ca. 235°C.

any indications of propylmercuric bromides. The above mixture appears definitely to consist of methyl- and ethyl-mercuric bromides (however, see later). By comparing the melting points of the fractions with those of known mixtures of methyl- and ethyl-mercuric bromides, they estimated that the ratio of methyl to ethyl radicals produced from butane was 7:3. Similar results were obtained with radicals from the pyrolysis of propane. Rice, Johnston, and Evering referred to a later publication by Rice and Whalley in which x-ray determinations were used to confirm the presence of methyl- and ethyl-mercuric bromides. The results of this work (248), however, seem rather equivocal.

Rice and Evering (232) repeated the above experiments and ran into considerable difficulty. They concluded that at least 95 per cent of the alkylmercuric bromides was methylmercuric bromide, and that ethylmercuric bromide was absent. The higher melting substance obtained in the previous work was presumably a small amount of mercuric bromide. In addition, they found that a trace of some unstable mercury alkyl is formed, probably $\text{CH}_3\text{HgHgCH}_3$. This is presumably the source of HgBr , a small amount of which was also detected. No indications of any methylene compounds were

obtained. Direct tests for the presence of ethyl groups were also made by a method developed by Willstätter and Utzinger (334), and these also were negative. Apparently then, only methyl radicals are detectable in the decomposition of propane and of butane. An improved technique for the identification of alkylmercuric halides has since been devised by Rice and Rodowskas (243). In this the mixture of alkylmercuric bromides and excess mercuric bromide is steam distilled. This effects a complete separation of the alkylmercuric bromides from the mercuric bromide, which is non-volatile under these conditions.

The fact that ethyl radicals are not detected in the decomposition means merely that higher radicals are unstable at high temperatures, and does not mean that the method is unsuitable for their detection. As a matter of fact, both ethyl and propyl radicals from photolyses have been identified by this technique by Pearson and his coworkers (209, 210). However, the above description will emphasize the difficulties encountered in work of this kind.

The products obtained from tellurium mirrors have also been widely employed for identification purposes, and have been the subject of much controversy. In particular, there has been much argument as to the existence of the methylene radical as deduced from evidence with tellurium and iodine mirrors. Since the question is of fundamental importance in connection with free-radical mechanisms, it will be reviewed in some detail, especially from the point of view of the occurrence or non-occurrence of the methylene radical in pyrolyses.

Rice and Glasebrook (235) investigated the free radicals produced from the decomposition of butane by means of tellurium mirrors, and found that the only detectable product was dimethyl ditelluride, $\text{CH}_3\text{TeTeCH}_3$. This is a deep red liquid with a low vapor pressure at room temperature; it is stable in air and melts at -19.5°C . This substance was recovered in almost theoretical yield in their experiments, and its composition was confirmed by combustion analysis. Similar results were obtained with radicals from acetone, in which case there is no doubt that methyl radicals are formed. This appears to confirm the idea that only methyl radicals are produced, ethyl and propyl radicals presumably being decomposed at the high temperatures used. They obtained no evidence of the presence of methylene.

Rice and Dooley (230) investigated the production of radicals when methane was decomposed at 1200°C . They obtained only pure dimethyl ditelluride, with no sign of telluroformaldehyde, $(\text{TeCH}_2)_x$, which would be expected if methylene radicals were present. This points definitely to the presence of methyl and the absence of methylene. (It is, of course, possible that the methyl radicals might be produced from methylene in secondary reactions.)

The methylene radical from the decomposition of diazomethane was identified by Rice and Glasebrook (230, 234), using tellurium mirrors. The product was a dark red solid of such low volatility that it condensed on the walls of the tube just beyond the mirror. Analysis showed it to have the empirical formula CH_2Te , i.e., it was telluroformaldehyde, probably in a highly polymerized state. The substance is insoluble in ordinary solvents, and decomposes at temperatures

above 100°C. It appears to be totally different from dimethyl ditelluride, and thus the use of tellurium offers a method of distinguishing between methyl and methylene radicals.

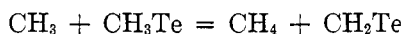
The work of Belchetz and Rideal is in sharp contrast to that of Rice and his coworkers. Belchetz (16), in a preliminary communication, reported that when methane was passed rapidly at a pressure of 0.1 mm. over a platinum filament at temperatures from 877° to 1027°C., tellurium mirrors situated one mean free path away were attacked. The products were collected in a liquid-air trap. Similar experiments were made with iodine mirrors. As a result of this work Belchetz concluded that methylene was the only primary product of the methane decomposition. Rice and Dooley were unable to obtain any mirror removal at such temperatures, even with platinum foil in their heated quartz tube. There seems to be little doubt that Belchetz' results were in error, since the temperatures used were impossibly low for a rapid-flow system unless there was a highly efficient catalytic effect due to the platinum. Also, as far as the identification of the products was concerned, Belchetz and Rideal were unable to confirm any of the results of the first paper. We may, therefore, disregard the results in the first paper and consider only Belchetz' later work.

Belchetz and Rideal (17) employed two different types of apparatus. In both of these the gas streamed through at a high velocity and at 0.1 mm. pressure. In the first the radicals formed on the hot filament were caught on a water-cooled target 3 mm. away. Mirrors could be deposited on this target, and any products formed were caught in a liquid-air trap. In the second apparatus the mirror was on the wall of the reaction vessel opposite the filament. It was considerably farther from the filament, and the system thus resembled the hot-tube type of apparatus employed by Paneth and by Rice. Tellurium and iodine mirrors were used, and carbon and platinum filaments. Methane was first investigated. With tellurium mirrors and platinum filaments, no volatile tellurium compounds were obtained. With platinum filaments and an iodine mirror, methylene iodide was formed.

Most of the work was done with carbon filaments. With iodine mirrors the identification of methylene iodide was claimed. This identification was attempted by two methods: In the first the substance was dissolved in chloroform, shaken with mercury to remove excess iodine, filtered, the chloroform evaporated off, and the product oxidized to formaldehyde and tested by the Schryver-Rimini test. For a minute quantity of material of dubious purity, such a complicated set of operations is hardly above suspicion. Attempts were also made to form mercury addition compounds, such as HgCH_2I_2 , and to identify them, but these were unsuccessful. No methyl iodide was found, the search for it being made merely by means of its volatility. When, however, the filament was moved 1 cm. from the mirror, the yield of methylene iodide became negligibly small, and an unidentified liquid which might have been methyl iodide made its appearance in traces in the trap. (This seems a very abrupt change on merely increasing the distance by a factor of 3, especially since the radicals were not in a heated zone.)

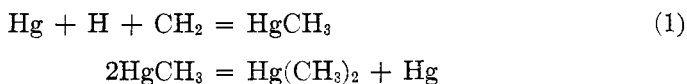
Experiments with tellurium mirrors were also carried out. With the second apparatus described, dimethyl ditelluride and dimethyl telluride were obtained. With the first apparatus the products were found to accumulate on the mirror, where they were exposed to further reaction. If the mirror was kept at 100°C., the products formed distilled off and were collected in the liquid-air trap. Under these conditions a trace of methyl tellurides was obtained, together with large quantities of a yellow solid which was assumed to be the telluroformaldehyde of Rice and Glasebrook. Belchetz and Rideal concluded, "These experiments indicate that methyl radicals are very readily produced in the flow experiments, but are essentially secondary products. Apart from the readiness with which methylene takes up atomic hydrogen, telluroformaldehyde is liable to be reduced by atomic or even possibly by hot molecular hydrogen."

The whole question is controversial, and other work of Belchetz and Rideal (18) also disagrees with Rice's findings. Thus with propane, using tellurium mirrors and carbon filaments, they found small amounts of dimethyl ditelluride and of telluroformaldehyde with warm tellurium mirrors, but only methyl tellurides with cold tellurium mirrors. They suggest that this is due to reduction of telluroformaldehyde by hydrogen when it remains in contact with a cold mirror, while with the warm mirror it evaporates off quickly and thus is not reduced. (There is also the possibility that with warm mirrors the reverse of this reaction might occur, i.e.,



or some such process.)

With mercury mirrors Belchetz and Rideal obtained large amounts of mercury alkyls, which with mercuric bromide gave CH_3HgBr . No ethylmercuric bromide was found, in agreement with the work of Rice and Evering. They attributed the formation of methylmercuric bromide to the sequence



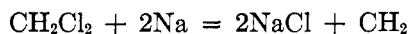
Reaction 1 seems exceedingly unlikely when the low pressure and very short reaction time are taken into consideration. Also, throughout all this work Belchetz and Rideal spoke of the atomic hydrogen present, but on the basis of their mechanism where does it come from? After all, there is no hydrogen in the reactant, and in one mean free path it cannot very well be formed by secondary processes.

Belchetz and Rideal concluded that, "In view of the experience of Rice and Glasebrook with the decomposition of diazomethane in the presence of butane or ether at temperatures above 650°C., when only methyl and no methylene radicals could be detected, it is not unlikely that all the methyl radicals formed in hot-tube decompositions of the hydrocarbons are in reality only secondary products of methylene."

It will be seen from the above that there are great difficulties in the unequivocal

identification of free radicals in some cases, and that considerable caution is necessary in the interpretation of the results. However, there seems to be no question that the methylene radical has been detected in certain cases.

Paneth and Lautsch (196) made numerous unsuccessful attempts to identify free methylene. These included the thermal decomposition of ketene and of diazomethane, an electrical discharge in diazomethane, and the reaction between dichloromethane and sodium (120):



All these attempts failed, but the failure was probably due to the detectors which they chose, namely, benzoic acid and carbon, neither of which would be expected to react very readily with methylene.

Rice and Glasebrook (233, 234) investigated the decomposition of diazomethane by their usual technique. Diazomethane with ether or butane as a carrier was passed through a tube at 550°C. or less, and then over mirrors. It was found that tellurium, selenium, arsenic, and antimony mirrors were readily removed, whereas zinc, cadmium, thallium, lead, and bismuth mirrors were not affected. In the case of tellurium mirrors the product was found to be a polymer of telluroformaldehyde, $(\text{TeCH}_2)_n$. This was a non-volatile red solid which condensed on the walls just beyond the mirror. At temperatures higher than 600°C. it was found that no telluroformaldehyde was produced, but only dimethyl ditelluride, $\text{CH}_3\text{TeTeCH}_3$, i.e., the methylene radicals were replaced by methyls. This work appears to give a very distinct test for methylene. The combustion data given to confirm the constitution of telluroformaldehyde were as follows:

	<i>Per cent carbon</i>	<i>Per cent hydrogen</i>
Calculated for CH_2Te	8.40	1.41
Found for CH_2Te	8.28	1.33

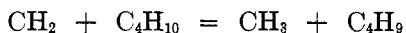
It should be noted, however, that on account of the high weight of the tellurium atom, virtually any organic tellurium compound would give a similar carbon analysis. The hydrogen analysis, though rather rough, is significant, since the per cent of hydrogen for the formula $\text{Te}_2(\text{CH}_3)_2$ would be 2.01. Actually, the calculated carbon value is in error, since the per cent of carbon for the formula CH_2Te is 8.47. The agreement is thus not quite as good as indicated above, although a small amount of occluded tellurium would account for the difference.

Rice and Glasebrook also found that at low temperatures no radicals were produced which would react with mercury to form mercury alkyls, but that at high furnace temperatures mercury dimethyl was formed.

They pointed out that telluroformaldehyde is so non-volatile that the compound found by Belchetz and Rideal cannot be it. Belchetz and Rideal suggested that in their work telluroformaldehyde came over as the monomer and polymerized in the trap. This, however, offers no explanation of the distinct difference between the compounds found in the two investigations.

Rice and Glasebrook concluded that the disappearance of methylene radicals

and appearance of methyl radicals at higher temperatures is satisfactorily explained provided the reaction



or the corresponding reaction with ether has an activation energy of about 15 ± 5 kcal.

In a review article Rice (228) referred to further unpublished work, carried out in collaboration with Bongiorno, which cast doubt on the work of Rice and Glasebrook described above. They reported as follows: "Cold diazomethane vapor appears to react with the tellurium vapor over a hot tellurium mirror to form telluro-formaldehyde. When experiments were performed under conditions such that this error was avoided, only methyl groups came out of the furnace. Thus even with pure diazomethane in pure nitrogen, methyl groups were obtained and carbon was deposited in the furnace." It appears from this work that Rice and Glasebrook's detection of the methylene radical was fallacious. However, the work of Bongiorno has never been published, a fact which suggests that it was not confirmed by later investigations.

A rather thorough investigation of this question was later made by Pearson, Purcell, and Saigh (211). They investigated both the thermal and the photochemical decomposition of ketene, using the mirror-removal technique. It was found that ketene irradiated with a hot or cold mercury arc had no effect on a cold tellurium mirror. However, if the mirror was heated to $70\text{--}80^\circ\text{C}$., it was readily removed. Blank experiments showed that this was not due either to evaporation or to an attack by ketene itself on the mirror. These authors suggested, as had others, that the necessity for heating the mirror is to prevent the formation on it of a layer of polymer.

They were unable to obtain the red telluroformaldehyde of Rice in a simple way. However, if the tube downstream from the mirror was cooled to -80°C ., the compound described by Rice was obtained (although they called it a deep orange, while Rice described it as red). It was found that the cooling was necessary only for seeding purposes, since if the tube was cooled for only a short time, the material continued to form where the cold spot had been.

Pearson, Purcell, and Saigh also obtained a gray substance which they took to be another modification of telluroformaldehyde. This, in solution with iodine, formed a substance which was fairly definitely proved to be methylene iodide. They also obtained evidence of the presence of an addition compound of the approximate constitution $\text{TeCH}_2 \cdot 12.5\text{CH}_2\text{CO}$. They concluded: "It is evident, therefore, that telluro-formaldehyde is first generated as a gas, which undergoes the familiar aldehydic condensations to a white form and a red form, the latter in view of its solubility being the higher polymer." They obtained no evidence of the presence of methyl radicals.

In a similar way selenium mirrors, even when cold, were readily removed with the formation of selenoformaldehyde.

The products from the thermal decomposition and the photodecomposition of diazomethane in the presence of tellurium mirrors were also investigated, and appeared to be telluroformaldehyde as before.

Pearson and coworkers concluded that, since one form of telluroformaldehyde is volatile, Rice's criticism of Belchetz and Rideal's results on the ground that it could not have escaped into the liquid-air trap cannot be upheld.

In a recent brief note (229) Rice described some further work. "We have attempted to obtain methylene from methane and other hydrocarbons by passage over heated filaments in an apparatus similar to that used by Belchetz and Rideal. Under their conditions for detecting methylene (Fig. 1 of reference 17), we succeeded in removing tellurium mirrors, but were unable to obtain enough tellurium compound to identify: we found that even after runs of several days, the amount of tellurium removed could not be weighed on an ordinary analytical balance. (Rice does not say whether the tellurium mirrors were heated or not.)

"On the other hand, by using much longer wires (Fig. 2 of reference 17) and larger mirrors, our results agreed with those reported by Belchetz and Rideal, and were similar to those obtained by passing methane through a quartz furnace; dimethyl ditelluride was obtained and identified by its melting point at -19.5°C ."

The whole question of the existence and identification of methylene has been reviewed by Barrow, Pearson, and Purcell (12). They reviewed the foregoing evidence at some length and concluded: "It seems to us that the fairest conclusion that can be drawn is that methylene as well as methyl may be one of the primary products in the dissociation of methane. Methylene radicals so formed may then undergo a rapid reaction with either methane, hydrogen, or another methylene radical, resulting in the production of methyl radicals. This cautious conclusion is dictated by our knowledge of the difficulties inherent in the unambiguous identification of products from experiments with filaments at low pressures, by the absence of quantitative data concerning the extent to which the dissociation of the hydrocarbons proceeds via a mechanism involving free radicals, and the equivocal nature of the evidence which may be adduced from kinetic experiments."

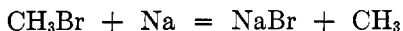
This seems a fair summing up of the situation as far as the detection of radicals is concerned. However, Barrow, Pearson, and Purcell overlook some of the kinetic evidence which is by no means "equivocal." In work with ethane, propane, and butane Belchetz and Rideal obtained in all cases an activation energy of *ca.* 94 kcal., and concluded that in every case the primary process was a direct molecular split and did not involve free radicals. This activation energy is much above the activation energies of the over-all thermal decompositions (60 to 70 kcal.). Now if free radical chains exist in these reactions, as postulated by Rice, there is every reason why the primary free radical split should have an activation energy 10 to 20 kcal. higher than that of the over-all reactions. If, however, as Belchetz and Rideal suggest, radicals are not involved, and the primary process is a direct molecular split into the final products, then there is no reason for the discrepancies in the activation energies. It therefore seems certain that in all of Belchetz and Rideal's work the carbon filament was a complicating factor, as they themselves realized. Furthermore, the fact that the activation energies are the same, within the experimental error,

for methane, ethane, propane, and butane suggests that the primary step is a direct reaction of some sort with the carbon filament. In any case, it appears clear that while Belchetz and Rideal's work may have a bearing on the question of the detection of the methylene radical, it has no bearing whatsoever on the homogeneous decomposition of hydrocarbons in the gas phase.

Barrow, Pearson, and Purcell also reviewed the evidence for ethylidene in the dissociation of ethane, in the light of the work of Rice and Dooley (230), who detected methyl radicals, and of Belchetz and Rideal who claimed ethylene and hydrogen as the primary products, possibly with ethylidene as an intermediate. In addition, there is evidence from work on the decomposition of diazoethane. Rice and Glasebrook (235) decomposed diazoethane at 650°C. and found no evidence of ethylidene, but rather of ethylene. Barrow, Pearson, and Purcell reported that at lower temperatures (400–450°C.) radicals were obtained which combined with selenium and tellurium to yield compounds with properties resembling those of seleno- and telluro-acetaldehydes. At 600°C., however, they obtained no mirror removal. It appears likely, therefore, that the ethylidene radical has been detected.

(c) Reactions in the gas phase

Free radicals have been detected by gas-phase reactions with the halogens in a number of cases. Thus Horn, Polanyi, and Style (130) formed methyl radicals by the reaction



The methyl radicals were then identified by introducing them into chlorine or iodine and identifying the methyl chloride or iodide formed. Similar experiments have been carried out with ethyl and phenyl radicals (129).

Gorin has used iodine to "fix" radicals and hydrogen atoms in a number of cases (103, 104, 105). In photolytic experiments iodine was mixed with the reactant. Any hydrogen atoms formed were "fixed" as hydrogen iodide, and alkyl radicals as methyl iodide, ethyl iodide, etc. In this way it was possible to determine the atoms or radicals formed in the primary reaction.

In a number of cases free radicals have been detected by the effects caused by their removal by gas-phase reactions. Nitric oxide has been the most widely used reagent for this purpose. Hinshelwood and his coworkers (127a, 128a, 128b, 281, 281a, 281b, 281c, 281d, 281e) have found that a number of reactions which are suspected to proceed by free-radical chain mechanisms are inhibited by the addition of small amounts of nitric oxide. The function of the nitric oxide is presumably to remove the radicals, and thus to prevent the further propagation of chains involving them. The nitric oxide probably forms an addition compound



On the assumption that small amounts of nitric oxide completely stop chain propagation, it is possible to calculate the chain length in the uninhibited reaction by the relation

$$\text{Chain length} = \frac{\text{Rate in absence of nitric oxide}}{\text{Rate in presence of nitric oxide}}$$

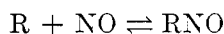
In the course of the reaction the nitric oxide is gradually consumed, but only very slowly. Thus, 2 mm. of nitric oxide can cut to about one-third the rate of decomposition of 400 mm. of ethyl ether, and yet last out the decomposition. The chain lengths found by this method in some typical cases are shown below:

CH₄.....4.7 at 850°C. and 100 mm.

C₂H₆.....17.8 at 600°C. and 100 mm.

C₆H₁₄.....1.9 at 530°C. and 100 mm.

Echols and Pease (59, 60) have investigated the inhibition of the butane decomposition by this method. Their results indicate that the inhibitory effect is only transient, but that this is not due to the removal of nitric oxide by reaction. Thus, with 200 mm. of butane and 20 mm. of nitric oxide at 520°C., the initial rate of reaction is almost zero. At 20 per cent decomposition, however, the rate is back to normal, and only 10 per cent of the nitric oxide has reacted. They suggest that there is an equilibrium



which is only slowly established.

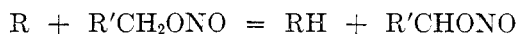
Forsyth (82a) has investigated the effect of nitric oxide on the concentration of methyl radicals by the Paneth technique, using tellurium mirrors, and has obtained a value of 6.5 kcal. for the activation energy of the reaction $CH_3 + NO = ?$.

There is a considerable number of experiments which seem to indicate (287) that the maximum inhibition attained in the presence of nitric oxide does not correspond to complete suppression of chains, and hence that the chain lengths calculated by this method are too low. However, there appears to be no doubt that inhibition by nitric oxide is usually a reliable criterion for the presence of free radicals in a system containing a decomposing organic substance.

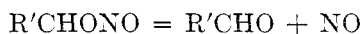
The nitric oxide inhibition method has also been used to detect radicals in the photolysis of mercury dimethyl (165, 322), azomethane (54), aldehydes (173a), and ketones (7a).

Taylor and Bender (307a) have recently investigated the pyrolysis of formaldoxime. They concluded that all the facts of nitric oxide inhibition can be explained on the assumption that a CH_2NO complex is initially formed and isomerizes into formaldoxime. The formaldoxime then decomposes and yields cyanides, ammonia, etc., which have been found by various workers in reactions inhibited by nitric oxide.

Methyl and ethyl nitrites have also been used to inhibit reactions in a similar way (241). In this case nitric oxide is produced *in situ* by the decomposition of the nitrites (243, 299, 300). Radicals are probably also removed by the reactions



and



Rice and Polly have also shown (241) that a number of organic decompositions are inhibited by propylene. Inhibition of hydrocarbon decompositions also occurs in the presence (66, 67) of "isobutene" (methylpropene), 2,2,4-trimethylpentene, divinyl, cyclohexene, and isoprene. Apparently the main requisite for inhibition in these cases is unsaturation, so that addition compounds may be formed with free radicals. It is well known that reactions of this type occur readily.

Oxygen has also been used as a detector for radicals and atoms. Locker and Patat added oxygen to formaldehyde in an investigation of its photolysis in order to detect free hydrogen atoms by reaction to form water (166, 198). Bates and Spence (13, 14) used oxygen similarly in the photolysis of alkyl halides. However, the possible reactions in these cases are too complicated for the method to yield reliable results.

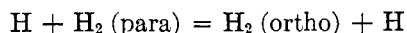
(d) The detection of hydrogen atoms by reaction with solids

Hydrogen atoms have been detected by their reducing action on solids such as copper oxides, dyes, etc., by a number of workers (see, e.g., 28, 29, 46, 325). The method, however, is not suited to quantitative application. For a very full list of compounds which are reduced by atomic hydrogen see Glockler and Lind (101).

2. *Spin-isomerism, isotopic labelling, etc.*

(a) The para-ortho hydrogen conversion

(1) *Determination of the hydrogen-atom concentration:* The equilibrium ratio of ortho- to para-hydrogen at temperatures from room temperature upwards is 3:1. At low temperatures, in the neighborhood of that of liquid hydrogen, the equilibrium corresponds to almost pure para-hydrogen, and by using charcoal as a catalyst for the conversion at low temperatures, para-hydrogen can thus be prepared. Para-hydrogen is stable at temperatures below *ca.* 500°C. for long periods, but the conversion to ortho-hydrogen at room temperature and up can be catalyzed by hydrogen atoms by the reaction

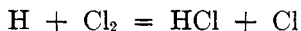


The kinetics of this reaction have been investigated by Geib and Harteck (94), using hydrogen atoms produced electrically, and by Farkas (70) with thermally produced atoms. The activation energy of the reaction is 6.7 kcal., with a steric factor of about 1/17 at room temperature, and of 1/7.5 at temperatures around 700°C.

Knowing the rate of the para-ortho conversion it is possible to calculate the hydrogen-atom concentration in a system which contains para-hydrogen by measuring the rate of the conversion. Thus, for example, Farkas and Sachsse (78) have determined the hydrogen-atom concentration in a system containing hydrogen and mercury, illuminated by the mercury resonance line, 2537 Å. Para-hydrogen was used in place of the ordinary equilibrium mixture. Samples

of hydrogen were withdrawn from time to time, and their para-ortho ratio was determined by measuring the thermal conductivity of the gas (71).

In simple systems the method is precise and yields unequivocal results (94). In more complex systems, however, difficulties are encountered in its application. In the first place the method cannot be used in a simple direct way unless the reaction by which the atoms normally disappear is considerably slower than the para-ortho conversion. Thus, the reaction

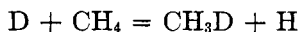


occurs roughly 10^4 times as fast as the para-ortho conversion catalyzed by hydrogen atoms at room temperature; hence it is only possible to determine the stationary hydrogen-atom concentration in the photochemical synthesis of hydrogen chloride by a special technique (278a).

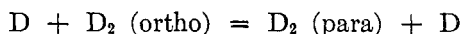
A further difficulty is the fact that the para-ortho conversion is catalyzed by all paramagnetic substances, such as oxygen, nitric oxide, and substances containing an odd number of electrons, i.e., all free radicals. Hence in complex systems it is always difficult to ascertain if the conversion observed is due to hydrogen atoms or to other atoms or radicals.

In the case of deuterium the situation is reversed. The high-temperature equilibrium corresponds to a para-ortho ratio of 2:1, and nearly pure ortho-deuterium can be prepared at low temperatures. Obviously the same technique can be applied with deuterium, and the rate of conversion of ortho- to para-deuterium can be used as a measure of the deuterium-atom concentration (71, 73, 74).

In the investigation of exchange reactions involving atomic deuterium, it is sometimes possible to interpret the kinetics of reactions by using ortho-deuterium and another substance, and making simultaneous measurements of the rates of conversion and exchange. For example, Farkas and Melville (75) produced deuterium atoms by photosensitization in mixtures of ortho-deuterium and methane, and made simultaneous measurements of the rates of the reaction



and

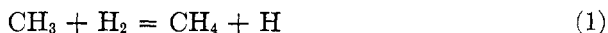


(2) *Determination of radical concentrations:* West (329) has made use of the fact that free radicals are paramagnetic, and should thus catalyze the para-ortho hydrogen conversion, to estimate radical concentrations. For example, methyl iodide was photolyzed in the presence of para-hydrogen, and it was found that the transitory products of the photolysis catalyzed the conversion. However, since atoms and other radicals also catalyze it, this cannot be regarded as a definite detection of the methyl radical (329a). West obtained similar results with acetone.

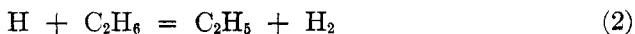
Rosenbaum and Hogness (256) found that the conversion was catalyzed by the products from decomposing hydrogen iodide. The rate was too fast to be

accounted for by catalysis by hydrogen atoms; hence it must have been catalyzed by iodine atoms as well.

Patat and Sachsse (199, 200, 202, 203, 258) have used an ingenious indirect method to measure radical concentrations and to test free-radical mechanisms by means of the para-ortho hydrogen conversion. For example, they measured the rate of the para-ortho hydrogen conversion in the presence of decomposing ethane, and were thus able to detect hydrogen atoms produced by the decomposition of ethane, or by the reaction



They assumed that the direct catalysis of the conversion by methyl radicals is negligible compared with the effect due to hydrogen atoms. If we accept the Rice-Herzfeld mechanism for the ethane decomposition (236), the hydrogen atoms produced by equation 1 are being destroyed mainly by the reaction



Hence the stationary concentration of hydrogen atoms is defined by the two processes, and we get approximately

$$\frac{(\text{CH}_3)}{(\text{H})} = \frac{k_2(\text{C}_2\text{H}_6)}{k_1(\text{H}_2)}$$

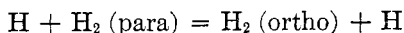
Having evaluated the hydrogen-atom concentration, we can compare it with that calculated from the Rice-Herzfeld mechanism. At 590°C. the experimentally found value is 10^{-11} mole per liter. The value predicted by the mechanism is about 1000 times larger, *viz.*, $10^{-8.2}$. This, therefore, appears to rule out the mechanism.

However, it is difficult to obtain unequivocal results by this method, since (a) the calculations depend strongly on the rate assumed for reaction 1, and are thus open to some question, and (b) the method can only yield results as to the truth or falsity of the Rice-Herzfeld mechanism in its detailed form, and depends completely on the activation energies assumed in this mechanism, especially for reaction 2 (see references 294, 295, and 296).

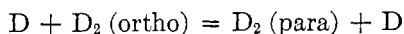
The method has been applied in a large number of cases by Patat and Sachsse, but it appears that its successful application demands a more detailed knowledge of the kinetics of the part reactions than is yet available in any given case.

(b) Exchange reactions

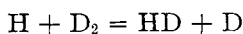
Just as the para-ortho hydrogen conversion



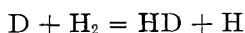
or



can be used as a measure of the stationary hydrogen- or deuterium-atom concentration in a system, so can the exchange reactions

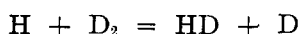


and



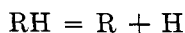
The kinetics of these reactions have been investigated by Farkas and Farkas (73). From their data the hydrogen- or deuterium-atom concentration in a system can thus be inferred from the rate of exchange. The extent to which the exchange has occurred can, like the para-ortho conversion, be inferred from thermal conductivity measurements.

An example of the use of this method is the investigation by Trenner, Morikawa, and Taylor (324) of exchange reactions of the paraffins by the Wood-Bonhoeffer method. In this work the deuterium-atom concentration in the system was determined by running hydrogen through the discharge, mixing the resulting $\text{H} + \text{H}_2$ with deuterium, and determining the extent to which the reaction

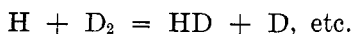


had occurred. The atom concentration was then calculated from Farkas and Farkas' results for this reaction, *viz.*, $E = 6.55$ kcal., $k_{299} = 4.9 \times 10^5$ liter mole sec., $s = 0.1$.

In many cases isotopic exchange reactions can be used to cast light on certain elementary processes. Usually this is done by rather detailed considerations of mechanism. One especially simple phenomenon which can be investigated in this way is the following: Suppose that in a photolysis the primary step appears to be



and that the quantum yield is low. It is desired to determine whether this is due to the back reaction proceeding efficiently, or to other causes. If deuterium is mixed with the reactant, then, owing to the reaction



there will also be deuterium atoms in the system. Hence if the back reaction proceeds readily, in addition to



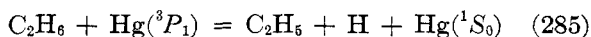
the reaction



will also occur. By analyzing the "unreacted" reactant for deuterium it is therefore possible to determine if the reverse of the primary step is the cause of the low quantum yield. Examples of the use of this procedure are the reactions



and



There are many other cases in which "tracer" experiments can thus shed light on primary processes. Not only deuterium, but also other isotopes, both stable and radioactive, have been used. A number of reviews of this type of work have appeared (92, 93, 226, 257).

3. Physical properties

(a) Diffusion

A fairly direct and reasonably accurate method of estimating the concentration of hydrogen atoms in a gas containing only H_2 and H has been devised by Wrede (340, 341) and Harteck (111). This can be used only at low pressures and for concentrations of atoms which are high enough to be of the same order of magnitude as that of the molecules. In practice, therefore, it is of use only with the discharge-tube method of producing hydrogen atoms.

In this method the stream of gas containing hydrogen atoms and molecules is led past a slit or capillary the width of which is smaller than the mean free path of the gas. For hydrogen at 1 mm. pressure this necessitates an opening with a width of about $1/20$ mm. Under these circumstances atoms or molecules pass through the capillary only by diffusion. On the outside of the capillary there are then both atoms and molecules. Inside the capillary, however, owing to recombination on the glass surface, or on platinum or some other metal which may be placed there, there are only molecules. As a result, in the steady state the pressure will be lower on the inside than on the outside, since atoms diffuse faster than molecules in the ratio $\sqrt{2}$, but one molecule passing through the capillary transports twice the mass of hydrogen taken through by an atom. Hence, for 100 per cent atoms outside, we have

$$\frac{\text{Pressure outside}}{\text{Pressure inside}} = 2/\sqrt{2} = 1.41$$

Similarly, for a volume per cent, n , of atoms,

$$n = \frac{100(P_1 - P_2)}{P_1(1 - 0.5\sqrt{2})}$$

where P_1 is the pressure on the outside, and P_2 that on the inside.

The pressure measurements are usually made with a Pirani gauge, since McLeod gauges have so large a volume that a very long time is required for pressure equilibrium to be established on account of the smallness of the capillary. The use of as small a gauge as possible is important, since pressure fluctuations inevitably occur in a flowing system. To speed up pressure equilibrium Chadwell and Titani (47) used a sintered-glass disc instead of a single orifice.

The fact that foreign gases must be absent is a distinct handicap, since in investigating atomic reactions measurements of the atom concentration must be made in blank runs when other reactants are not present. The ideal case for the use of the method is in the investigation of the para-ortho hydrogen conversion, since in this case the above limitation does not exist.

While the method has occasionally been used for oxygen or nitrogen atoms, it is not very satisfactory since the mean free path at the same pressure is much smaller in these cases, and finer capillaries must therefore be used. As a result the establishment of equilibrium is extremely slow. In spite of these drawbacks it has been used successfully for chlorine by Rodebush and Klingelhofer (252).

Poole (217) has criticized all determinations with Wrede gauges on the ground that it is doubtful whether some mass-flow through the orifice has not occurred.

The method is inapplicable to free radicals, since systems containing them are always too complex.

(b) Calorimetry

Calorimetric methods of detecting and estimating hydrogen atoms have been frequently employed. The method is obviously attractive in principle, since the recombination of hydrogen atoms may be very easily brought about on catalyst surfaces, and the recombination is exothermic to the extent of approximately 103 kcal. per mole.

Calorimetric detection was first employed by Bonhoeffer (28), who coated thermometer bulbs with various substances and found that considerable temperature rises occurred. This method has also been used by Taylor and Lavin (315). Thermocouples have been employed in a similar way (213).

The use of glowing wires as a test for hydrogen atoms has been reported by Wood and by a number of later workers (see, e.g., 325). In this method the heat of recombination on a metal wire acting as a catalyst is sufficient to bring the wire to incandescence and thus afford a visual indication of the presence of atoms. One difficulty with this method is that the wire frequently becomes "poisoned." In one modification of the method (284) the wire is maintained at a just visible red heat (at which temperature poisoning does not occur) by the passage of a current. In the presence of atoms recombination heats the wire, and less current is necessary to maintain it at the same temperature. The decreased wattage is then a direct measure of the heat received from recombining atoms. The method is rough, but convenient.

More accurate calorimetric methods have been used by a number of workers (7, 25, 55, 276, 328). In all of these a catalyst mass is placed in the reaction tube at the place where the atom concentration is to be measured, and the heat received by the catalyst is measured by noting the temperature rise and applying cooling corrections, etc. The main difficulty is to correct for the loss by gaseous conduction, which is quite high and amounts to as much as 50 per cent of the observed temperature rise.

Objections to calorimetric methods have been raised on the grounds that the introduction of an efficient catalyst which causes complete removal of atoms sets up a diffusion of atoms towards the catalyst and thus alters the normal atom concentration throughout the reaction tube (7, 217, 301, 303, 328). However, it appears that with proper care in experimental arrangements this is not serious.

Poole (217) has recently described a continuous-flow calorimeter which seems to meet the objections which have been raised to the method, and which greatly cuts down conduction losses.

Schwab and Friess (267) have used the heating of a copper-constantan thermocouple as a method of determining chlorine atoms. This was used only for relative measurements. For absolute measurements they used a calorimeter consisting of a thin metal plate in which a thermocouple was imbedded. This

was heated by atom recombination, and was calibrated by heating electrically in blank experiments.

Schwab (264) has also used the heating of a thermocouple to measure the relative concentration of bromine atoms produced by the discharge-tube method.

There are indications that heating of a wire by recombination may have successfully indicated the presence of hydroxyl radicals (325).

(c) Thermal conductivity

Senftleben and Germer (268) detected chlorine atoms in chlorine illuminated with light in the region of the continuum by means of the increased thermal conductivity of the gas. Senftleben and Riechemeier (268a) in a similar way have measured the stationary hydrogen-atom concentration in mercury-hydrogen mixtures illuminated with λ 2537.

(d) Pressure change

In a few cases the increase in pressure on dissociation of a molecule into atoms (or the decrease on their recombination) has been used as a qualitative or quantitative indication of the presence of atoms. Thus, by a special technique Smallwood (277) was able to compress very quickly a mixture of hydrogen molecules and atoms from a discharge, and to follow the recombination process by measuring the pressure with a diaphragm gauge with photographic recording.

In the case of chlorine and bromine, the well-known Budde effect (38) indicates the production of atoms by the rise in pressure obtained when photochemically produced chlorine atoms recombine and give out heat.

(e) Mass spectrograph

Early attempts to use the mass spectrograph as an analytical tool (187a) were complicated by the electron dissociation of the parent molecule, but Eltenton (60a) has recently taken advantage of the fact that the ionization potentials of free radicals are lower than the appearance potentials of the same ions produced by electron dissociation. In contrast to the results of Belchetz and Rideal, he found methyl radicals but no methylene radicals in the decomposition of methane. He was also able to detect methyl and ethyl radicals in the decomposition of ethane, methylene from diazomethane, and allyl radicals in the reaction of methyl radicals with propylene.

4. Optical methods

(a) Emission spectra

"Emission spectra cannot serve as a quantitative measure of the concentration of free radicals since, for the appearance of an emission spectrum, not only the occurrence of free radicals but also their excitation is necessary" (126). The same remarks obviously apply to atoms as well. Even from a qualitative point of view, emission spectra cannot in general be used as an indication of the presence of atoms or radicals, except in a few special cases (see below) or where

high energies are involved (as in discharges, flames, or in photochemistry of the Schumann region), so that any radicals formed are in excited states and thus emit radiation.

In discharges, etc., a large number of radicals have been detected, such as C_2 , CH, CN, NH, OH, PH, and ions of various sorts. (For reviews of this subject see references 26, 101, 126, and 280.) In flames and explosions C_2 , CH, OH, NH, and probably CHO and other radicals have been observed (32, 89a, 93a, 98a, 132, 134, 163, 323, 325a). In the Schumann region a considerable number of atoms and radicals have been detected in emission during photolyses (see, for example, references 182, 220, 342).

Resonance emission has been used in a number of cases to detect and measure the concentration of atoms and of unstable molecules. Hartel and Polanyi (120) followed the changes in the concentration of sodium atoms in reaction mixtures by illuminating with sodium resonance radiation (the D line) and measuring the intensity of the resonance radiation emitted.

In a qualitative way the presence of HgH in mercury-hydrogen mixtures illuminated with λ 2537 (23) and of CdH and ZnH in the corresponding experiments with cadmium and zinc (19, 187) has been established by the resonance emission of HgH, CdH, and ZnH bands. It should be noted that the successful detection of atoms or radicals by the resonance emission of lines or bands originating on the ground state depends on the atoms or radicals being in the ground state rather than in excited states.

Bay and Steiner (11) have used emission spectra to measure atom concentrations in a Wood's tube. A pair of subsidiary electrodes were placed in the reaction tube, and a weak high-frequency discharge was passed between them. By observing this spectrographically and determining the ratio of the intensities of certain atomic lines to molecular bands, it was possible to use the method as a relative measure of the atom concentration. Or, by running calibration experiments against a Wrede gauge, the spectroscopic observations could be made to give absolute values of atom concentrations.

(b) Absorption spectra

In principle the detection and estimation of atoms and radicals in absorption is without difficulty. In practice, however, it is necessary that the concentration be fairly high for this method to be successful. (See reference 186 for a discussion of the difficulties involved.)

Bonhoeffer and Reichardt (37) photographed the hydroxyl bands in absorption in a flow system with steam at temperatures in the neighborhood of 1600°C., and were thus able to determine the equilibrium in the reaction



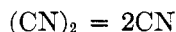
Bonhoeffer and Pearson, however, were unable to find the hydroxyl radical in absorption in the gas flowing from a discharge through water vapor (36). Geib and Harteck (113) were also unable to find it spectroscopically in the reaction of hydrogen atoms with oxygen.

Oldenberg (87, 184, 185, 304), by using a 21-ft. grating, found the hydroxyl radical in absorption in a discharge in water vapor. He was able to detect it for as long as 1/8 sec. after the discharge was interrupted.

The hydroxyl radical has frequently been found in absorption in hydrogen and hydrocarbon flames (9, 33, 134, 144, 145, 146, 147, 148, 163).

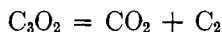
Franck and Reichardt (83) detected the NH radical in absorption in a flow system in decomposing ammonia at 2000°C.

Kistiakowsky and Gershinowitz (139, 140) and White (332a) investigated the dissociation of cyanogen,



in the neighborhood of 1200°C. by using absorption spectroscopy with a flow system.

The C₂ radical was detected in absorption by means of the Swan bands in the reaction



by Klemenc, Wechsberg, and Wagner (142).

For a review of the detection of CH and other radicals in absorption see Willey (333).

Rabinowitsch and his coworkers (221, 222, 223) have measured the atom concentration in illuminated systems containing the halogens by measuring the extinction coefficients, and from these calculating the decrease in the number of molecules present, and hence indirectly the atom concentration.

Hydrogen-atom concentrations have also been measured by absorption (217a).

(c) Miscellaneous optical methods

Kohanenko (143) has detected radicals and atoms by means of a glowing screen of zinc sulfide, as described previously.

In investigating the reaction between mercury vapor and the halogens, Ogg, Martin, and Leighton (183) used light from a resonance lamp to cast a shadow of a mercury-vapor jet, and thus followed the decrease in concentration of the mercury vapor by a method analogous to the diffusion flame technique. In this way they were able to follow relatively fast reactions with activation energies of the order of 5 kcal.

Kudrjawzewa and Prileshajewa (149) used an ingenious method to investigate the photodecomposition of adsorbed acetone. The acetone was adsorbed on a thin metallic mirror, and a spectrum was focussed on it. The photochemically effective light formed radicals which removed the mirror at the part of the spectrum which was effective. In this way the photochemical threshold for adsorbed acetone was determined.

5. Inference

In practice the presence of radicals, their concentration, etc., is often arrived at by inference from investigations conducted by ordinary methods. Thus the

mechanism of a reaction may be arrived at, sometimes with considerable certainty, by conclusions based on rates of formation of stable products as determined by pressure change, analysis, etc., and by the effect of temperature, pressure, etc. on these rates. If a mechanism can be established by such means, radical concentrations and the rates of elementary reactions can then be calculated. This is frequently a very useful method, although it can hardly be classed as an investigation of the elementary processes in question.

Another method of arriving at the activation energies of elementary reactions which is frequently employed makes use of the fact that the heat of the reaction is equal to the difference between the activation energies of the forward and the reverse reactions. The heat of the reaction can, in turn, be calculated from a knowledge of the strengths of the bonds formed and broken in the reaction. Hence if we know the activation energy of a reaction and the strengths of the bonds involved, we can estimate the activation energy of the reverse process. The difficulty is that there is usually no very certain knowledge of the bond strengths.

III. SUMMARY OF METHODS

In conclusion it may be well to summarize the main methods of investigation discussed above, from the point of view of reliability, errors, etc.

A. THERMAL DECOMPOSITION—STATIC OR FLOW METHODS

From such investigations valuable information is usually obtained. However, from a radical or atom point of view all information is obtained strictly by inference, and is thus correspondingly uncertain.

B. THERMALLY SENSITIZED DECOMPOSITIONS

This type of investigation gives very definite information whether or not radicals react with a substance under certain defined conditions, and whether free-radical chains are set up. However, the results are usually quite indefinite as to what the reaction is between the radicals and the substrate.

C. INHIBITION

This gives definite information regarding the occurrence or non-occurrence of free-radical chains in the decomposition. It gives rather dubious information about the lengths of such chains. It gives, however, no information about the nature of the reactions involved.

D. THE PANETH-RICE METHOD

This is much the most direct method in so far as the detection and identification of radicals are concerned. However, this detection is difficult, and in certain cases, notably methylene *versus* methyl, the results are equivocal. The method furnishes reliable values of the activation energies of the split of stable molecules into radicals at high temperatures. It is not, however, well adapted to the determination of the rates or activation energies of other types of radical reactions.

E. THE BELCHETZ-RIDEAL TECHNIQUE

This appears to have definite merit as far as the detection of *primary* products is concerned. However, the present status of work done by this method is somewhat uncertain, and a reinvestigation would be of decided value.

F. DILUTE FLAMES AND DIFFUSION FLAMES

The main advantage of these methods is their applicability to very fast reactions. They appear to be among the most reliable methods as far as atomic reactions are concerned. The extension of the methods to free radicals produces such complex systems that the results obtained are rather indirect, and are much less certain.

G. PARA-ORTHO HYDROGEN CONVERSION

The use of this method to determine the hydrogen-atom concentration in simple systems undoubtedly gives reliable results. In more complex systems it is impossible to decide to what extent the conversion obtained is due to other paramagnetic substances. The Sachsse-Patat modification of the method is too dependent on a detailed knowledge of the mechanism of the processes which are occurring to be of much value.

H. THE WOOD-BONHOEFFER METHOD

As a means of producing atoms, this is the best of all methods, since a definite high concentration results. The further reaction steps are arrived at by inference from the final products, and are thus on much less certain ground. Surface effects are also a source of considerable uncertainty. A combination of this method with the Paneth-Rice technique appears to offer interesting possibilities.

I. PHOTOLYSIS

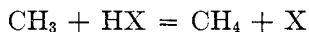
The results of photolytic experiments suffer from the same uncertainties as those of thermal reactions, since a detailed mechanism must be established from a consideration of the *final stable products of the reaction and their variation with pressure, temperature, light intensity, etc.* The rates of elementary reactions are then deduced from this mechanism. However, there is one distinct advantage over thermal reactions: namely, that the primary step may be definitely established from spectroscopic data.

J. THE PEARSON TECHNIQUE

This gives very definite information as to the *presence* of radicals in photo-decompositions. The identification is often definite, but is difficult, since the quantities of material to be analyzed are in general even smaller than with the ordinary Paneth method. The method is only suitable for the detection and identification of the primary products of photolyses.

K. SENSITIZATION BY RADICALS PRODUCED BY PHOTOLYSIS

This method, especially in the form employed by Taylor and his collaborators, gives very direct information concerning the rates of reaction of radicals with molecules. The main difficulty is the possibility that, for example, in a reaction



methane may be formed by reactions other than the one being investigated.

L. PHOTSENSITIZATION BY METAL VAPORS

This is a very useful method of producing hydrogen atoms. As compared with the Wood-Bonhoeffer method, however, it is much more difficult to determine the stationary hydrogen-atom concentration.

In the case of other reactions the difficulty is that, as with photolysis, a mechanism must first be established by inference, and the rates of elementary reactions then deduced from such a mechanism. The primary step is not as easy to establish as in photolytic experiments, but it can usually be well established if sufficient quenching information is available.

M. EXCHANGE REACTIONS

These give much useful information. This is not a real "method," however, since it must always be combined with one of the foregoing.

Difficulties and uncertainties

It may be said that no single investigation of an elementary reaction has ever been made which is free from ambiguity. The only possible procedure is the accumulation of data, and the testing of mechanisms by consideration of their compatibility with results obtained by various experimental methods. In conclusion it may again be pointed out that the activation energies of elementary reactions are never *measured*, but are calculated from the temperature coefficients of processes the nature of which must be arrived at by indirect means.

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