Reactions of Radicals in Gaseous Systems.

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In the last 25 years it has become apparent that free radicals play a major part in most gas-phase reactions of simple organic molecules. There is no question that most photochemical reactions of this type involve radicals. The work of Sir Cyril Hinshelwood and his school makes it probable that hydrocarbon decompositions do not proceed entirely by a free-radical mechanism, but certainly free radicals play a prominent part in these reactions and in other organic decompositions.

Rice has proposed a type of mechanism for organic decompositions which is certainly largely valid in principle. There are, however, many discrepancies in specific cases. As a result it has become very important to investigate the chemical reactions of organic free radicals in the gas phase. If the rates of such reactions could be determined unambiguously it would be possible to make many detailed predictions about the overall mechanisms of organic reactions.

The main problem in investigating the rates of free-radical reactions is that the radicals have to be prepared *in situ*, and there is thus some uncertainty about their identity, purity, and especially their concentration. It is usually impossible to determine radical concentrations directly, and it is therefore necessary to compare ratios of rates, or to use some indirect yardstick as a measure of the radical concentration. In general, photochemical methods of producing radicals for such investigations are to be preferred since it is possible in this way to vary the temperature independently of the rate of production of radicals, and to work at much lower temperatures. The investigation of the rates of elementary organic reactions has therefore become one of the major tasks of photochemistry.

Types of Elementary Reaction.—A typical Rice mechanism (which is certainly over-simplified) is that for the ethane decomposition :

$$C_2H_6 \longrightarrow 2CH_3 \tag{1}$$

$$CH_3 + C_2H_6 \longrightarrow CH_4 + C_2H_5 \tag{2}$$

$$C_2H_5 \longrightarrow C_2H_4 + H \tag{3}$$

$$H + C_2H_6 \longrightarrow C_2H_5 + H_2 \tag{4}$$

$$H + C_2H_5 \longrightarrow C_2H_6 \tag{5}$$

$$\text{or} \longrightarrow C_2H_4 + H_2 \tag{6}$$

There are thus several distinct types of free-radical reaction which need investigation. Reaction (1) is essentially a question of bond dissociation energies. Reaction (3) is a radical decomposition. Reactions (2) and (4) are metatheses which involve the transfer of a hydrogen atom from a molecule to a radical. Reactions (5) and (6) involve the recombination and disproportionation of two radicals. In this lecture I propose to review the present status of our knowledge of hydrogen-transfer reactions, recombination, and disproportionation.

The Acetone Photolysis.—In choosing a substance as a photochemical source of radicals it is obviously desirable to pick one whose photochemical behaviour has been well investigated. A favourite choice is acetone, which, following on the pioneer work of Norrish, has been much investigated by Noyes and his collaborators. Acetone absorbs from about 3300 Å down to shorter wavelengths. It is too complex a molecule to be very promising from a spectroscopic point of view, and I will not discuss its spectrum, or its very interesting fluorescence properties. Its photochemical decomposition has been much investigated between 3130 Å and 2537 Å. The list of free-radical reactions which are definitely involved in its photolysis is formidable, *viz.*,

$$CH_3{\cdot}CO{\cdot}CH_3 + h\nu \longrightarrow CH_3 + CH_3{\cdot}CO \tag{7}$$

$$CH_3 + CH_3{\cdot}CO \longrightarrow CH_3{\cdot}CO{\cdot}CH_3 \tag{8}$$

$$CH_3 + CH_3 \longrightarrow C_2H_6 \tag{9}$$

$$CH_3{\cdot}CO + CH_3{\cdot}CO \longrightarrow (CH_3{\cdot}CO)_2 \tag{10}$$

$$CH_3{\cdot}CO \longrightarrow CH_3 + CO \tag{11}$$

$$CH_3 + CH_3{\cdot}CO{\cdot}CH_3 \longrightarrow CH_4 + CH_2{\cdot}CO{\cdot}CH_3 \tag{12}$$

$$CH_3 + CH_2{\cdot}CO{\cdot}CH_3 \longrightarrow C_2H_5{\cdot}CO{\cdot}CH_3 \quad \ldots\ldots \quad (13)$$

$$2CH_2{\cdot}CO{\cdot}CH_3 \longrightarrow (CH_2{\cdot}CO{\cdot}CH_3)_2 \quad \ldots\ldots \quad (14)$$

$$CH_2{\cdot}CO{\cdot}CH_3 \longrightarrow CH_2{\cdot}CO + CH_3 \quad \ldots\ldots \quad (15)$$

$$CH_3 + CH_3{\cdot}CO \longrightarrow CH_4 + CH_2{\cdot}CO \quad \ldots\ldots \quad (16)$$

$$CH_3{\cdot}CO + CH_3{\cdot}CO \longrightarrow CH_3{\cdot}CHO + CH_2{\cdot}CO \quad \ldots\ldots \quad (17)$$

The usual way of dealing with such a mechanism is the so-called steady-state method. In this we equate the rate of change of concentration of the short-lived species to zero in the steady state and solve the resulting equations. This has two disadvantages in the present case. In the first place the mechanism must be complete, and we are by no means certain that there are no other part reactions involved. Also, with 11 part reactions the resulting equations would be exceedingly complex and impossible to apply to the results.

The situation is not, however, nearly as bad as it looks. Reaction (8) merely lowers the quantum yield, and provided we are dealing with ratios of products it can be neglected. Acetyl is unstable, and at temperatures above 100° or 120° it is legitimate in the absence of highly reactive added substances to write (7) as

$$CH_3{\cdot}CO{\cdot}CH_3 + h\nu \longrightarrow 2CH_3 + CO \quad \ldots\ldots \quad (7a)$$

and to neglect all reactions involving $CH_3{\cdot}CO$, *viz.*, (8), (10), (11), (16), and (17). Also, reaction (15) is only of importance at quite high temperatures. Hence in the range 100—300° it is almost always permissible merely to write the mechanism as :

$$CH_3{\cdot}CO{\cdot}CH_3 + h\nu \longrightarrow 2CH_3 + CO \quad \ldots\ldots \quad (7a)$$

$$CH_3 + CH_3 \longrightarrow C_2H_6 \quad \ldots\ldots \quad (9)$$

$$CH_3 + CH_3{\cdot}CO{\cdot}CH_3 \longrightarrow CH_4 + CH_2{\cdot}CO{\cdot}CH_3 \quad \ldots\ldots \quad (12)$$

$$CH_3 + CH_2{\cdot}CO{\cdot}CH_3 \longrightarrow C_2H_5{\cdot}CO{\cdot}CH_3 \quad \ldots\ldots \quad (13)$$

$$2CH_2{\cdot}CO{\cdot}CH_3 \longrightarrow (CH_2{\cdot}CO{\cdot}CH_3)_2 \quad \ldots\ldots \quad (14)$$

It may, however, be profitable to give a word of warning about simplified mechanisms at this point. All possible part reactions will always occur to some extent. In certain circumstances it will be possible to ignore many of them. It should be emphasized, however, that the resultant simple mechanisms will only hold over limited ranges of the experimental parameters. One should always be cautious in applying a simple mechanism when the conditions have been drastically changed with regard to temperature, concentration, intensity, presence of foreign gases, and so on.

Hydrogen-abstraction reactions.

In the temperature range 100—300° a mass of information has been obtained about hydrogen-abstraction reactions by the following method. In this range the only reaction forming ethane is (9) and the only reaction forming methane is (12). Hence, where R_x represents the rate of formation of the product x, and Ac represents acetone,

$$R_{C_2H_6} = k_9[CH_3]^2$$

$$R_{CH_4} = k_{12}[CH_3][Ac]$$

Hence $$k_{12}/k_9^{\frac{1}{2}} = R_{CH_4}/(R_{C_2H_6}{}^{\frac{1}{2}}[Ac])$$

It is thus possible to evaluate $k_{12}/k_9^{\frac{1}{2}}$. If now a foreign gas RH is added, methane will also be produced by

$$CH_3 + RH \longrightarrow CH_4 + R \quad \ldots\ldots \quad (18)$$

Hence, provided that there is still no other method of forming CH_4 and C_2H_6,

$$R_{CH_4} = k_{12}[CH_3][Ac] + k_{18}[CH_3][RH]$$

$$R_{C_2H_6} = k_9[CH_3]^2$$

Hence $$R_{CH_4}/R_{C_2H_6}{}^{\frac{1}{2}} = k_{12}[Ac]/k_9^{\frac{1}{2}} + k_{18}[RH]/k_9^{\frac{1}{2}}$$

Since $k_{12}[\mathrm{Ac}]/k_9^{\frac{1}{2}}$ is known, we can evaluate $k_{18}/k_9^{\frac{1}{2}}$. It thus becomes possible to determine the rates of reaction (18) for a series of organic compounds relative to the rate of recombination of methyl radicals. Actually, as we shall see later, the rate of recombination of methyl radicals has now been determined, so that it is possible to arrive at absolute values of the rate constants of reactions of the type of (18).

An alternative approach is to use deuteroacetone, and compare the rate of (19) with that of (20).

$$CD_3 + CD_3{\cdot}CO{\cdot}CD_3 \longrightarrow CD_4 + CD_3{\cdot}CO{\cdot}CD_2 \quad . \quad . \quad . \quad . \quad . \quad (19)$$

$$CD_3 + RH \longrightarrow CD_3H + R \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (20)$$

By these methods the rates of a large number of hydrogen-abstraction reactions have been measured in recent years.[1] By carrying out the investigation over a range of temperatures we can determine the activation energy and the pre-exponential factor as expressed by the Arrhenius equation $k = Ae^{-E/RT}$, or, if we put $A = PZ$, where Z is the collision number and P is the so-called steric factor, the results can be given in the form of activation energies and steric factors.

A few typical results for a series of hydrocarbons are given in Table 1. Recent unpublished results by Kutschke indicate that some of the activation energies in the Table are somewhat low, as are the steric factors. The differences are not great enough to change the trend of the results, although they somewhat increase the scatter. The differences in A and E compensate one another, however, and the rate constants at a given temperature are little affected.

TABLE 1. *The abstraction of hydrogen atoms by methyl radicals from the photolysis of acetone.*
(Trotman-Dickenson and Steacie.[2])

Compound	$E_{18} - \frac{1}{2}E_9$ (kcal.)	$k_{18}/k_9^{\frac{1}{2}} \times 10^{13}$ * at 182° c.	$P_{18}/P_9^{\frac{1}{2}} \times 10^4$	Number of " active " H- atoms	$k_{18}/k_9^{\frac{1}{2}} \times 10^{13}$ * at 182° c. per " active " H-atom
Ethane	10·4	3·8	6	6	0·6
2 : 2-Dimethylpropane	10·0	6·3	6	12	0·5
2 : 2 : 3 : 3-Tetramethylbutane	9·5	10·0	7	18	0·6
n-Butane	8·3	21	3	4	4·5
n-Pentane	8·1	27	3	6	4·0
n-Hexane	8·1	33	3	8	3·8
2-Methylpropane	7·6	42	3	1	37
2 : 3-Dimethylbutane	7·8	78	6	2	36
2 : 3 : 4-Trimethylpentane	7·9	65	8	3	20
Ethene	10·0	5·6	9	4	1·4
Propene	7·7	23	3	3	8
But-2-ene	7·7	57	7	6	10
2-Methylpropene	7·3	49	4	6	8
2 : 3-Dimethylbut-2-ene	7·8	145	17	12	12
But-1-ene	7·6	66	8	2	33
Pent-1-ene	7·6	68	8	2	34
3-Methylbut-1-ene	7·4	102	9	1	102
*cyclo*Propane	10·3	2·1	4	6	0·4
*cyclo*Butane	9·3	22	17	8	2·8
*cyclo*Pentane	8·3	47	9	10	4·7
*cyclo*Hexane	8·3	42	8	12	3·7
Benzene	9·2	1·9	1	6	0·3
Toluene	8·3	26	5	3	8·7
Acetone	9·7	19	10	6	3·2

* Units of quantities entering into k are molecules, cm.^{3}, and seconds.

One result that is apparent is that the steric factors of these reactions are low, of the order of 10^{-3}. It has frequently been assumed in the past that such steric factors are approximately unity. It is obvious that this is not the case, and that the mere determination of an activation energy gives only a very vague idea of the value of the corresponding rate constant at any temperature. The determination of the rate constant involves an accurate experimental determination of both A and E.

The results in Table 1 show clearly the effect of chemical structure. As far as the paraffins

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[1] Steacie, " Atomic and Free Radical Reactions," Reinhold Pub. Corp., New York, 1954.

[2] Trotman-Dickenson and Steacie, *J. Chem. Phys.*, 1951, **19**, 329.

[3] Whittle and Steacie, *ibid.*, 1953, **21**, 993.

are concerned, it is evident that the activation energy for the removal of a hydrogen atom from a primary carbon atom is greater than that for secondary, which in turn is greater than that for a tertiary carbon atom. Unfortunately, errors in E and P compensate each other and it is difficult to get sufficient accuracy to make a detailed treatment of structure significant. The values of the absolute rates at a given temperature, shown in col. 3 of the Table, are much more reliable. It will be seen that there is the same trend, hydrogen atoms attached to tertiary atoms being the most reactive, followed by those on secondary and then primary as would be expected from chemical evidence.

A surprisingly good correlation is obtained if one takes the rate constant " per active H-atom." Thus for ethane there are six hydrogen atoms on primary carbon atoms. If the value in col. 3 is divided by 6 we obtain $0{\cdot}6 \times 10^{13}$ as the value of $k_{18}/k_9^{\frac{1}{2}} \times 10^{13}$ at 182° c. In a similar way for 2 : 2-dimethylpropane, with 12 hydrogen atoms on primary carbon atoms, and 2 : 2 : 3 : 3-tetramethylbutane with 18, we obtain 0·5 and $0{\cdot}6 \times 10^{13}$. The values in the last column show very striking differences between hydrogen atoms on primary, secondary, and tertiary carbon atoms.

In the case of the olefins a similar correlation is obtained if we consider the nature and number of the hydrogen atoms in an α-position to the double bond. Here again the order of reactivity is tertiary > secondary > primary.

The cyclic hydrocarbons again yield results in line with the chemical evidence. The rates of abstraction from *cyclo*pentane and *cyclo*hexane, where there is little strain in the ring, are almost exactly the same as that for a secondary hydrogen in a paraffin.

Again, as expected, toluene is much more reactive than benzene. Actually, however, the difference is perhaps less than one might expect in view of the frequently assumed great difference in bond dissociation energies between the ring and side-chain hydrogen atoms.

Other Radical Sources.—A considerable number of investigations have been made in which other sources of methyl radicals have been used from which it is possible to get similar information about reactions of the type $CH_3 + RH \longrightarrow CH_4 + R$. This furnishes a very valuable check on the results given in Table 1. A number of such results are given in Table 2. It is

TABLE 2. *Results with various sources of methyl radicals.*[1]

Reactant	Radical source	E (kcal.)	k at 182° c. $\times 10^{-6}$ (mole^{-1} cm.^{3} sec.$^{-1}$)
2-Methylpropane	Acetone	7·6 ± 0·2	22
	$Hg(CH_3)_2$	7·3 ± 0·3	16
	Azomethane	6·7 ± 0·3	10
Toluene	Acetone	8·3 ± 0·3	14
	$Hg(CH_3)_2$	7 ± 2	5
	DTBP *	11 ± 2	—
Methanol	Acetone	8·2 ± 0·2	6
	$Hg(CH_3)_2$	8·2 ± 0·5	5
Ethyleneimine	DTBP *	4·8 ± 0·3	200
Azomethane	Azomethane	7·6	~20
Dimethyl ether	Acetone	9·5 ± 0·2	9
	$Hg(CH_3)_2$	8·4 ± 1·5	9
	$CH_3{\cdot}O{\cdot}CH_3$	10 ± 2	12
n-Butane	Acetone	8·3 ± 0·2	11
	$Hg(CH_3)_2$	8·2 ± 0·5	22
	$Hg(CH_3)_2$	9·5 ± 0·5	10
	$Hg(CH_3)_2$	—	13
	Azomethane	9·1 ± 0·3	—
*cyclo*Propane	Acetone	10·3 ± 0·4	1·1
	$Hg(CH_3)_2$	10·2 ± 1·0	1·5
Ethylene oxide	$Hg(CH_3)_2$	9·0 ± 1·0	1·5
	$Hg(CH_3)_2$	9·6 ± 2	2·8
Acetaldehyde	DTBP *	8·0 ± 0·3	220
Acetone	Acetone	9·7 ± 0·1	10
	Acetone	9·6 ± 0·4	8
	Acetone	9·5 ± 0·2	11
	DTBP *	9·5 ± 1·0	9
Diacetyl	Diacetyl	7·1 ± 0·2	17
Di-*tert.*-butyl peroxide	DTBP *	(15)	2
Dimethylmercury	$Hg(CH_3)_2$	9·0 ± 0·5	10
	$Hg(CH_3)_2$	11·0	3
Dimethylcadmium	$Cd(CH_3)_2$	(14)	2

* DTBP = Di-*tert.*-butyl peroxide.

evident that, in general, the agreement between different workers, using different sources of radicals, is excellent. In particular, the rate constants at a given temperature are almost always in agreement to within a factor of 1·5. This agreement indicates strongly that the results are not in error because of errors in mechanism, and there is no reason to suspect the participation of " hot " radicals.

Isotope Effects.—Since deuterium tracer methods have been largely used in the investigation of methyl-radical reactions, it is important to consider isotope effects. The more clear-cut case is the group of reactions of the type $CH_3 + H_2 \longrightarrow CH_4 + H$, and we will consider this as an example. The effects to be expected are not large compared with experimental errors, and since errors in E and A are compensating, it is difficult to obtain reliable results. We will therefore confine our attention to absolute values of rate constants at a given temperature, since these are much more accurate. Results are given in Table 3.

The main point which is evident from the Table is that reactions involving the breaking of the stronger D–D bond are considerably slower than those involving the H–H bond. On the other hand, there is relatively little difference between reactions of CH_3 and of CD_3.

Higher Alkyl Radicals.—There is not much information about the hydrogen-abstraction reactions of higher alkyl radicals. Since $D(C_2H_5\text{–}H)$ is 4—5 kcal. less than $D(CH_3\text{–}H)$, hydrogen abstraction by ethyl radicals will be 4—5 kcal. less exothermic than the corresponding reactions with methyl radicals. This might be expected to be reflected in higher activation energies. Table 4 gives most of the relatively few data which are available.

TABLE 3. *Reaction of methyl radicals with hydrogen isotopes.*

(Whittle and Steacie.[3])

Reaction	$k_A/k_B^{1/2} \times 10^{13}$ * at 210° c.	Reaction	$k_A/k_B^{1/2} \times 10^{13}$ * at 210° c.
$CH_3 + D_2 \longrightarrow CH_3D + D$ ...	7·85	$CH_3 + HD \longrightarrow CH_4 + D$ ...	9·1
$CH_3 + H_2 \longrightarrow CH_4 + H$ ...	22·0	$CH_3 + HD \longrightarrow CH_3D + H$	5·1
$CD_3 + H_2 \longrightarrow CD_3H + H$ ...	26·5	$CD_3 + HD \longrightarrow CD_3H + D$	10·4
$CD_3 + D_2 \longrightarrow CD_4 + D$	8·9	$CD_3 + HD \longrightarrow CD_4 + H$ ...	6·0

* k_A is the rate constant of the hydrogen-abstraction reaction, k_B that of the recombination of methyl radicals.

TABLE 4. *Hydrogen-abstraction by ethyl radicals.*

Substance	E (kcal.)	P (approx.)	Ref.	Substance	E (kcal.)	P (approx.)	Ref.
$Hg(C_2H_5)_2$	6·2	1×10^{-4}	4	D_2	13·4	10^{-3}	6
$CO(C_2H_5)_2$	7·4	3×10^{-4}	5	$C_2H_5{\cdot}N{:}N{\cdot}C_2H_5$	7·4	10^{-3}	7
$CH_3{\cdot}CO{\cdot}C_2H_5$	8·0	1×10^{-4}	8				

Few data exist on hydrogen abstraction by radicals higher than ethyl. The abstraction of hydrogen from azo*iso*propane by *iso*propyl radicals[9] and that from di-*n*-propyl ketone by *n*-propyl radicals[10] both have activation energies of about 6·5 kcal. The reaction $Pr^i + H_2 \longrightarrow C_3H_8 + H$ has an activation energy of about 12·5 kcal.[11]

It appears, therefore, that there is on the whole not much difference in reactivity between methyl, ethyl, and propyl radicals in spite of the difference in heats of reaction. This emphasizes the danger of assuming a parallelism between heats of reaction and activation energies. An extreme case of the absence of such a parallelism is the series of reactions

$$CH_3 + CH_4 \longrightarrow CH_4 + CH_3 \qquad CH_3 + H_2 \longrightarrow CH_4 + H \qquad CH_3 + HCl \longrightarrow CH_4 + Cl$$

The bond dissociation energies of CH_4, H_2, and HCl are all identical to within ±1 kcal., but the activation energies are respectively about 12, 10, and 5 kcal.

Reactions of Trifluoromethyl Radicals.—Some recent work by Ayscough has given interesting results on the reactions of CF_3 radicals. If hexafluoroacetone is photolysed the mechanism is,

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[4] Ivin and Steacie, *Proc. Roy. Soc.*, 1951, *A*, **208**, 25.
[5] Kutschke, Wijnen, and Steacie, *J. Amer. Chem. Soc.*, 1952, **74**, 714.
[6] Wijnen and Steacie, *J. Chem. Phys.*, 1952, **20**, 205.
[7] Ausloos and Steacie, *Bull. Soc. chim. belges*, 1954, **63**, 87.
[8] *Idem*, *Canad. J. Chem.*, 1955, **33**, 1062.
[9] Durham and Steacie, *ibid.*, 1953, **31**, 377.
[10] Masson, *J. Amer. Chem. Soc.*, 1952, **74**, 4731.
[11] Hoey and LeRoy, *Canadian J. Chem.*, 1955, **33**, 580.

deactivation of excited molecules being neglected, *i.e.*, only those molecules which decompose being considered:

$$CF_3{\cdot}CO{\cdot}CF_3 + h\nu \longrightarrow 2CF_3 + CO \qquad (21)$$

$$2CF_3 \longrightarrow C_2F_6 \qquad (22)$$

The reaction is thus extraordinarily simple. The simplicity by comparison with the decomposition of ordinary acetone appears to arise from two facts. In the first place, $CF_3{\cdot}CO$ is too unstable to be a complication. Secondly, because of the very strong C–F bonds, the reaction

$$CF_3 + CF_3{\cdot}CO{\cdot}CF_3 \longrightarrow CF_4 + CF_2{\cdot}CO{\cdot}CF_3$$

does not appear to occur, at least at temperatures up to 120° c. If now a hydrocarbon RH is added, the reactions

$$CF_3 + RH \longrightarrow CF_3H + R \qquad (23)$$

$$CF_3 + R \longrightarrow CF_3R \qquad (24)$$

$$2R \longrightarrow R_2 \qquad (25)$$

will occur. A determination of CF_3H and C_2F_6 then enables us to make use of the relations $R_{C_2F_6} = k_{22}[CF_3]^2$ and $R_{CF_3H} = k_{23}[CF_3][RH]$, and hence

$$k_{23}/k_{22}^{\frac{1}{2}} = R_{CF_3H}/(R_{C_2FH}^{\frac{1}{2}}[RH])$$

It is thus possible to determine values of $k_{23}/k_{22}^{\frac{1}{2}}$ for a series of hydrocarbons, RH. Since Ayscough has made a direct determination of k_{22}, the rate constant for the recombination of radicals, by a sector method,[12] it is possible to calculate absolute values of k_{23} at various temperatures. Actually, the rate of recombination of CF_3 radicals is very little different from that of CH_3 radicals. In Table 5 the results for CF_3 reactions are compared with those for CH_3 for a number of hydrocarbons. Some very recent results obtained by Pritchard, Pritchard, and Trotman-Dickenson [12a] are in excellent agreement with the values in Table 5.

In spite of certain discrepancies in the values for CH_3, there is no question that CF_3 reacts with a lower activation energy and much more rapidly than does CH_3.

All in all, the general state of our knowledge regarding metathetical reactions of this type appears to be fairly satisfactory, but more information is badly needed on the reactions of complex radicals.

TABLE 5. *Rate of reactions of the type* $CF_3 + RH \longrightarrow CF_3H + R$.[13]

Reaction	$k_A/k_R^{\frac{1}{2}} \times 10^{13}$ * at 400° K. (cm.$^{3/2}$ mol.$^{-\frac{1}{2}}$ sec.$^{-\frac{1}{2}}$)	$P_A/P_R^{\frac{1}{2}}$ (400° K.)	E_A (kcal.)	$k_A \times 10^{18}$ at 400° K. (cm.^{3} mol.$^{-1}$ sec.$^{-1}$)
$CH_3 + CH_4$	0·029	6×10^{-4}	13—14	0·017
$+ C_2H_6$	0·83	3×10^{-4}	10·4	0·49
$+ C_3H_8$	—	—	—	—
$+$ *n*-C_4H_{10}	5·8	3×10^{-4}	8·3	3·42
$+$ *iso*-C_4H_{10}	12·6	3×10^{-4}	7·6	7·43
$CF_3 + CH_4$	3·5	6×10^{-3}	10·3	2·19
$+ C_2H_6$	104	6×10^{-3}	7·5	65
$+ C_3H_8$	418	6×10^{-3}	6·5	261
$+$ *n*-C_4H_{10}	631	2×10^{-3}	5·1	395
$+$ *iso*-C_4H_{10}	1010	2×10^{-3}	4·7	631

* k_A refers to the abstraction reaction and k_R to the radical-recombination reaction in each case.

Recombination and disproportionation of radicals.

Another type of reaction to which I should like to give some attention is that involving the interaction of two radicals, *i.e.*, recombination and disproportionation. It is only within the last five or six years that any quantitative information has been available about this type of process, but the present situation appears to be fairly satisfactory.

In considering the recombination of free radicals two factors are concerned. One of these

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[12] Ayscough, *J. Chem. Phys.*, 1956, **24**, 944.

[12a] Pritchard, Pritchard, and Trotman-Dickenson, *Chem. and Ind.*, 1955, 564.

[13] Ayscough, Polanyi, and Steacie, *Canad. J. Chem.*, 1955, **33**, 743; Ayscough and Steacie, *ibid.*, 1956, **34**, 103.

is the well-known third-body restriction on recombination reactions. This may be expected to hold stringently for the recombination of two atoms, and to be of little importance in the case of the recombination of two complex radicals which have many internal degrees of freedom to take care of the excess of energy. In the second place we may expect true steric factors to cut down the efficiency of the recombination for very complex radicals. It is therefore quite uncertain *a priori* what the efficiency will be for intermediate cases such as the recombination of methyl and ethyl radicals.

In considering the mechanism of recombination, one method is to treat the reaction as bimolecular ($2CH_3 \longrightarrow C_2H_6$), with an efficiency which varies with pressure. A more detailed mechanism involves the formation of a complex and its dissociation or stabilization, *i.e.*,

$$2CH_3 \longrightarrow C_2H_6{}^*$$

$$C_2H_6{}^* \longrightarrow 2CH_3$$

$$C_2H_6{}^* + M \longrightarrow C_2H_6 + M$$

where M is any third body. Recombination is, of course, merely the reverse of unimolecular dissociation. For the moment we will consider the process as a straight bimolecular reaction, and see what the collision efficiency is at ordinary pressures. Later we will come back to the effect of pressure.

In the case of methyl radicals three methods of investigation have been used. The first is to compare the rate of the reaction $CH_3 + CH_3 \longrightarrow C_2H_6$ with that of some other known reaction of methyl, in this case $CH_3 + NO \longrightarrow (CH_3{\cdot}NO)$. The rate of the latter reaction is known from experiments of the Paneth mirror-removal type. A second method involves the use of a mass-spectrometer to follow the decay of the methyl-radical concentration directly. The third method is the well-known intermittent light, or sector, method which has been widely used to determine radical lifetimes in polymer chemistry. This is by far the simplest and most accurate method. The first two methods give results which are in every way compatible with the sector method, and we will limit further discussion to the last method.

The Sector Method.—This method has been widely used, and I will not discuss the general theory here. There are, however, certain differences in its application, since we are not dealing with a chain reaction in the present case. The use of the sector method depends on the fact that the rate of a photochemical reaction with intermittent light is different from that with continuous illumination of the same total intensity. Such a condition will exist whenever the rate of the reaction is proportional to a power of the light intensity other than the first.

It is easy to see why this is the case. Suppose that methyl radicals are being produced photochemically; then the concentration of radicals will be greater the higher the intensity. Suppose now that they disappear from the system by two reactions and that the rates are

$$R_1 \propto [CH_3]$$

$$R_2 \propto [CH_3]^2$$

At high light intensities R_2 will gain on R_1. Hence R_1 will increase by a power of the intensity less than unity. (Actually in this case $R_1 \propto I^{\frac{1}{2}}$.)

Suppose that we consider the simplest possible case which might be used to measure the rate of recombination,

$$X + h\nu \longrightarrow 2CH_3 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

$$CH_3 + CH_3 \longrightarrow C_2H_6 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

If we could measure the stationary concentration of methyl radicals, then k_2 would follow immediately, since in the steady state

$$d[CH_3]/dt = 0 = 2I - k_2[CH_3]^2$$

Unfortunately, we can only measure the rate of production of stable products. In these circumstances the method will not work, since from the above we have

$$[CH_3] = (2I/k_2)^{\frac{1}{2}}$$

$$d[C_2H_6]/dt = k_2[CH_3]^2 = k_2 \,.\, 2I/k_2 = 2I$$

Hence every CH_3 formed gives C_2H_6 eventually, and the rate is proportional to I, not to $I^{\frac{1}{2}}$.

Gomer and Kistiakowsky,[14] who first investigated the methyl recombination by a sector method, got round the difficulty by using a pilot reaction as a competitor for CH_3. Thus, suppose we have

$$CH_3 + X \longrightarrow CH_4 + Y \quad . \; . \; . \; . \; . \; . \; . \; . \; . \quad (3)$$

One can then treat the system very simply by adjusting conditions so that (3) occurs only to the extent of 2 or 3% as compared with (2). In these circumstances $[CH_3]$ is not greatly affected by (3), and we still have

$$[CH_3] \sim (2I/k_2)^{\frac{1}{2}}$$

Hence $$d[CH_4]/dt = k_3[X][CH_3] = k_3[X](2I/k_2)^{\frac{1}{2}}$$

i.e., the rate of production of CH_4 is proportional to $I^{\frac{1}{2}}$ and the sector method can be applied by following the rate of formation of CH_4 as a function of sector speed. (Actually, it is not necesary to use the above approximation, as the theory for the complete mechanism has been worked out in practical form by Kutschke and Dainton, Burnett and Wright, and Shepp.[14a])

Gomer and Kistiakowsky produced methyl radicals by the photolysis of dimethylmercury and of acetone, and used as " pilot reactions " the hydrogen-abstraction reactions

$$CH_3 + CH_3{\cdot}CO{\cdot}CH_3 \longrightarrow CH_4 + CH_2{\cdot}CO{\cdot}CH_3$$

or $$CH_3 + Hg(CH_3)_2 \longrightarrow CH_4 + CH_2{\cdot}Hg{\cdot}CH_3$$

In this way they found the values given in Table 6.

Table 6.

(Pressure = 10—50 mm.)

Radical source	Temp. (°c.)	k_2 (cm.^{3} mole^{-1} sec.$^{-1}$)	Radical source	Temp. (°c.)	k_2 (cm.^{3} mole^{-1} sec.$^{-1}$)
Acetone	125°	$4{\cdot}5 \times 10^{13}$	Dimethylmercury	175°	$4{\cdot}6 \times 10^{13}$
Acetone	175	$4{\cdot}2 \times 10^{13}$	Dimethylmercury	250	$6{\cdot}7 \times 10^{13}$

The rate constants correspond to recombination at approximately every collision of two methyl radicals.

The Effect of Pressure on the Recombination of Methyl Radicals.—Two investigations have been made recently, by Kistiakowsky and Roberts [15] and by Dodd and Steacie,[16] in which the effect of pressure on the recombination has been studied in detail by photolysing acetone at low pressures. Kistiakowsky and Roberts extended the experiments of Gomer and Kistiakowsky. At a pressure of 10 mm. the rate constant for the recombination of methyl radicals was found to be $3{\cdot}7 \times 10^{13}$ cm.^{3} mole^{-1} sec.$^{-1}$, corresponding to a collision efficiency of about unity. There is thus good agreement with Gomer's work. The rate constants decreased with pressure down to 1 mm., the lowest pressure studied. The decrease in rate was in agreement with a mechanism in which the rate becomes dependent on the stabilization of an excited complex by collision with a third body. Thus for the mechanism we may write

$$CH_3{\cdot}CO{\cdot}CH_3 + h\nu \longrightarrow 2CH_3 + CO \quad . \; . \; . \; . \; . \; . \; . \quad (4)$$

$$CH_3 + CH_3{\cdot}CO{\cdot}CH_3 \longrightarrow CH_4 + CH_2{\cdot}CO{\cdot}CH_3 \quad . \; . \; . \; . \; . \quad (5)$$

$$CH_3 + CH_3 \longrightarrow C_2H_6{}^* \quad . \; . \; . \; . \; . \; . \; . \; . \; . \; . \quad (6)$$

$$C_2H_6{}^* \longrightarrow 2CH_3 \quad . \; . \; . \; . \; . \; . \; . \; . \; . \quad (7)$$

$$C_2H_6{}^* + CH_3{\cdot}CO{\cdot}CH_3 \longrightarrow C_2H_6 + CH_3{\cdot}CO{\cdot}CH_3 \quad . \; . \; . \; . \quad (8)$$

Their results fit such a mechanism excellently and indicate a decrease of a factor of 3 to 4 in the recombination rate constant over the pressure range 10—1 mm.

[14] Gomer and Kistiakowsky, *J. Chem. Phys.*, 1951, **19**, 85.

[14a] Kutschke, James, and Dainton, unpublished work; Burnett and Wright, *Proc. Roy. Soc.*, 1954, *A*, **221**, 37; Shepp, *J. Chem. Phys.*, 1956, **24**, 939.

[15] Kistiakowsky and Roberts, *ibid.*, 1953, **21**, 1637.

[16] Dodd and Steacie, *Proc. Roy Soc.*, 1954, *A*, **223**, 283.

Dodd and Steacie investigated the acetone photolysis with steady illumination down to a presssure of about 0·1 mm., and inferred the fall in the rate of recombination at lower pressures from the changing value of the ratio $k_5/k_2^{\frac{1}{2}}$.

The results of both investigations may be treated in the following way. If it is assumed that in the acetone photolysis methane comes only from reaction (5) and ethane from (2), then for second-order recombination

$$\rho = \frac{k_5}{k_2^{\frac{1}{2}}} = \frac{R_{CH_4}}{R_{C_2H_6}^{\frac{1}{2}}[CH_3{\cdot}CO{\cdot}CH_3]}$$

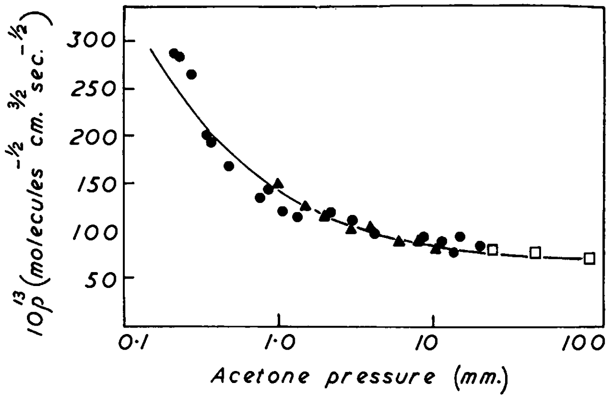
If recombination occurs by a third-order process

$$2CH_3 + CH_3{\cdot}CO{\cdot}CH_3 \longrightarrow C_2H_6 + CH_3{\cdot}CO{\cdot}CH_3 \quad . \ . \ . \ . \quad (9)$$

then

$$r = \frac{k_5}{k_9^{\frac{1}{2}}} = \frac{R_{CH_4}}{R_{C_2H_6}^{\frac{1}{2}}[CH_3{\cdot}CO{\cdot}CH_3]^{\frac{1}{2}}}$$

FIG. 1.



In the intermediate region, similarly,

$$\rho = \frac{k_5}{k_6^{\frac{1}{2}}}\left(\frac{k_5}{k_6[CH_3{\cdot}CO{\cdot}CH_3]} + 1\right)^{\frac{1}{2}}$$

and reduces to $k_5/k_6^{\frac{1}{2}}$ at high pressures. At lower pressures the ratio will rise. This is shown by Fig. 1.

Similarly, in the intermediate range

$$r = \frac{k_5}{k_6^{\frac{1}{2}}}\left(\frac{k_7}{k_8} + [CH_3{\cdot}CO{\cdot}CH_3]\right)^{\frac{1}{2}}$$

At low pressures this will reduce to a constant value. Fig. 2 shows the results plotted in this way. There is thus excellent agreement between all investigations and there seems to be no doubt that the recombination is becoming strongly pressure-dependent at low pressures. At the lowest pressures there is also some evidence of heterogeneity.

The effect of foreign gases on the recombination has also been investigated. Kistiakowsky and Roberts found that carbon dioxide was only about 1/40 as efficient as acetone as a third body. Dodd found the following approximate efficiencies relative to acetone:

Argon	<0·03	Benzene	1·0
Carbon dioxide	0·03	(Acetone)	(1·0)
Decafluorobutane	0·2	Acetaldehyde	3·0
Perfluoromethyl*cyclo*hexane	0·3		

Ethyl Radicals.—The reaction of two ethyl radicals is more complex than that of two methyls, since in addition to recombination to form butane, disproportionation to ethane and ethylene

FIG. 2.

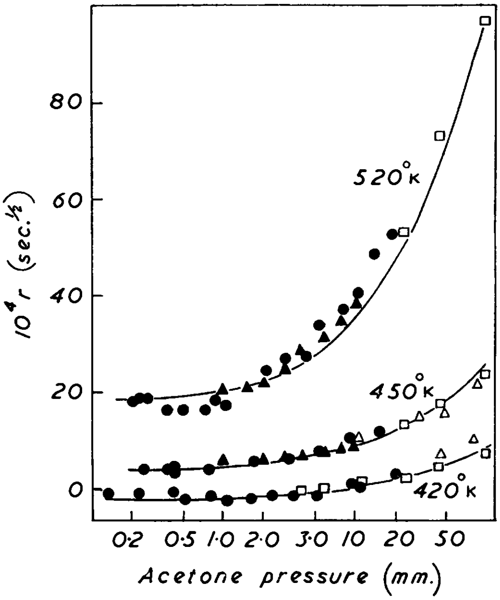
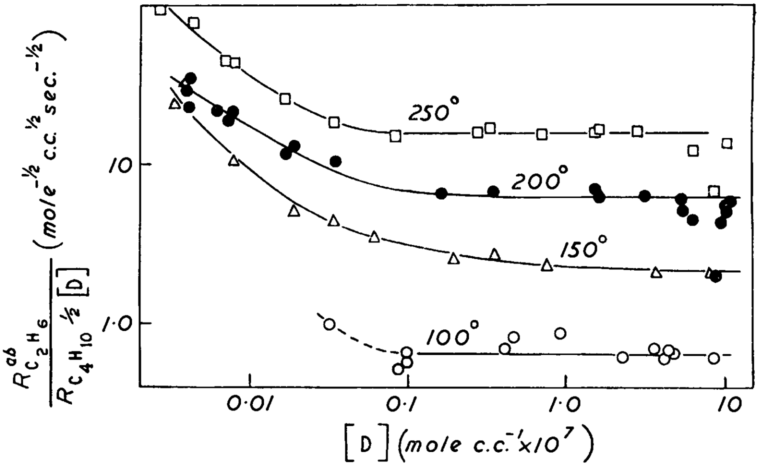


FIG. 3.



also occurs. The best investigated case is that of the diethyl ketone photolysis, the main steps in the mechanism of which are :[5]

$$C_2H_5\cdot CO\cdot C_2H_5 + h\nu \longrightarrow 2C_2H_5 + CO \quad (10)$$

$$2C_2H_5 \longrightarrow C_4H_{10} \quad (11)$$

$$2C_2H_5 \longrightarrow C_2H_6 + C_2H_4 \quad (12)$$

$$C_2H_5 + C_2H_5\cdot CO\cdot C_2H_5 \longrightarrow C_2H_6 + C_2H_4\cdot CO\cdot C_2H_5 \quad (13)$$

$$C_2H_5\cdot + C_2H_4\cdot CO\cdot C_2H_5 \longrightarrow C_4H_9\cdot CO\cdot C_2H_5 \quad (14)$$

$$2C_2H_4\cdot CO\cdot C_2H_5 \longrightarrow (C_2H_4\cdot CO\cdot C_2H_5)_2 \quad (15)$$

$$C_2H_4\cdot CO\cdot C_2H_5 \longrightarrow C_2H_4 + CO + C_2H_5 \quad (16)$$

Conditions can be adjusted so that reaction (16) is unimportant. In these circumstances the determination of the rate of formation of ethylene makes it possible to differentiate between ethane formed by (12) and by (13). Measurements by the sector method with diethylmercury[4] and diethyl ketone[17] indicate that reaction (11) occurs with a collision efficiency of the order of 0·1 at higher pressures. The fact that the efficiency is below 1 may be due merely to the uncertain meaning of collision cross-sections, or it may indicate a real steric effect for the more complex ethyl radicals.

Brinton has recently investigated the photolysis of diethyl ketone at low pressures.[18] Fig. 3 shows the results treated in the same way as for methyl radicals above. It will be seen that no third-body effects are noticeable down to 0·1 mm. or less. Below this pressure heterogeneous processes complicate the situation. It is found, however, that down to 0·01 mm. or less there is no change in the ratio k_{12}/k_{11}. It seems most unlikely that the disproportionation reaction (12) would show a pressure effect. It therefore seems probable that reaction (11) is independent of pressure down to at least 0·01 mm.

Conclusion.

Considerable progress has been made in the last ten years in building up a chemistry of free radicals in the gas phase. There remains, however, much to be done. Our knowledge of bond dissociation energies is still far from satisfactory in most cases. Also there is much interest today in combustion and in other processes involving oxygen-containing radicals. This is a very difficult field, and as yet not a great deal has been accomplished. It is, however, a field of very great importance, and major advances are to be expected within the next few years.

[17] Shepp and Kutschke, *J. Chem. Phys.*, in the press.

[18] Brinton and Steacie, *Canad. J. Chem.*, 1955, **33**, 1840.