The Structure and Reactivity of Free Radicals.

THE TILDEN LECTURE DELIVERED BEFORE THE CHEMICAL SOCIETY ON NOVEMBER 11TH, 1948.

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ONE of the outstanding achievements of the study of chemical kinetics has been the demonstration that many apparently complex chemical changes occur in a sequence of stages, each of which is characterised by extreme simplicity. Many of these are chain reactions involving atoms or radicals formed by the breaking of chemical bonds, and experiment has shown that the various stages in the chain are the most elementary types of reaction involving the transfer of an electron or an atom from one reactant to the other.

The thermal decomposition and oxidation of hydrocarbons, or the formation and breakdown of addition polymers, are typical of reactions which involve the participation of intermediary free radicals. The initiation of these processes by the formation of an atom or radical sets in motion the sequence of elementary reactions which lead to the final stable products. It is evident that the complete unravelling of this sequence, and the formulation of the rates and energy changes of the simple reactions which make up the complete picture, would not only enable us to predict quantitatively the course and rate of any change, but would also constitute the basis of a theory of chemical reactivity. Recent progress in the study of radical reaction has taken us some way towards this goal. It is with these general principles of radical reactions rather than the detailed consideration of any particular class of chain-reaction that I wish to deal.

The characteristic property of a free radical is that it carries an unpaired electron, and this electron is available for the formation of a bond with another radical, or atom or group of a molecule. This immediately gives us a convenient classification of radical reactions: (*a*) inter-radical reactions, and (*b*) reactions of radicals with molecules.

Inter-radical Reactions.

When two radicals come together, alternative reaction possibilities exist. Either they combine together to give a saturated molecule, or an atom transfer occurs with the formation of a saturated and an unsaturated molecule, *e.g.*:

$$C_2H_5 + C_2H_5 \longrightarrow C_4H_{10} \quad . \; . \; . \; . \; . \; . \; . \; . \; . \; . \; . \quad (1)$$

$$\longrightarrow C_2H_6 + C_2H_4 \quad . \; . \; . \; . \; . \; . \; . \; . \quad (2)$$

Reactions of this type are those which lead to the destruction of radicals and are chain-terminating processes. It is because they are usually the terminating process of a reaction sequence that it has been a matter of some difficulty to decide experimentally the relative probabilities of (1) and (2) and to specify the rates of these processes. Recently, by the use of the technique of highly attenuated flames (Polanyi, " Atomic Reactions," Williams and Norgate, 1932; Bawn, *Ann. Reports*, 1942, **39**, 36), it has been possible to prepare radicals in a relatively pure state, free from reactive partners, and to study the kinetics of these simple reactions.

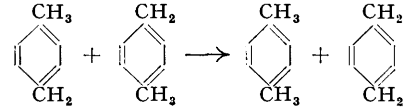
Under these conditions (in the temperature range 280—380°) it has been found that, with alkyl radicals, disproportionation is a relatively easy process and requires little or no activation (Bawn and Tipper, Faraday Soc. Discussion, " Labile Molecules," 1947, p. 104) *e.g.*:

$$\begin{array}{llll} CH_3 + CH_3 & \longrightarrow CH_4 + CH_2. & E = 8 \text{ k.-cals.} \\ C_2H_5 + C_2H_5 & \longrightarrow C_2H_6 + C_2H_4. & E = \sim 0 \text{ k.-cals.} \\ C_3H_7 + C_3H_7 & \longrightarrow C_3H_6 + C_3H_8. & E = \sim 0 \quad ,, \end{array}$$

These conclusions are strongly supported by the corresponding reactions in solution. By studying the reactions of radicals prepared by the dissociation of silver alkyls (−60° to 0°) (Bawn and Whitby, *ibid.*, p. 228), $AgCH_3 \longrightarrow Ag + CH_3$, and $AgC_2H_5 \longrightarrow Ag + C_2H_5$, it has been shown that methyl radicals recombine entirely to give ethane, whereas ethyl radicals largely disproportionate. Under the same conditions of preparation, both radicals initiate the polymerisation of vinyl acetate.

In thermal reactions, disproportionation is invariably accompanied by extensive recombination, and the activation energies of the above reactions are evaluated on the assumption that the activation energy for recombination is zero. The latter value has not been measured directly for simple radicals, and various values for E have been assigned to this reaction. The weight of evidence is now in favour of $E_{\text{recomb.}} = 0$ for simple alkyl radicals. It has been frequently stated that, since methyl is planar whilst in ethane the structure is tetrahedral, the transition which occurs when the radicals join up would require an appreciable activation energy. Calculation, however, shows that attraction between the two free carbon orbitals in flat methyl, even at relatively large distances, is greater than the H–H repulsions. The flat radicals thus attract each other at large distances, and the hydrogens slip over to the tetrahedral configuration without activation.

The corresponding reactions between simple aryl radicals are particularly interesting since, with one notable exception, dimerisation seems to proceed exclusively. For example, in investigations of highly attenuated flames, phenyl, benzyl, and benzoyl give dimers, and recently Szwarc and his collaborators (*J. Chem. Physics*, 1948, **16**, 128, 981) have shown by thermal-decomposition studies that *o*- and *m*-xylyl radicals and the fluoro-*o*-, -*m*-, and -*p*-tolyl radicals dimerise. The exception is *p*-xylyl which disproportionates to give a biradical :

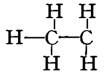


The reason for this will be considered later.

Thermal Stability.—In any thermal reaction there is superimposed upon the effects of recombination and disproportionation the tendency of the radicals to decompose. Thus the tendency of the alkyl radicals to split up into a radical and an olefin increases with increase in chain length. A consideration of this factor leads to an interesting series of radical stabilities. The dissociation of methyl according to $CH_3 \longrightarrow CH_2 + H$ requires energy of the order of the C–H bond strength in methyl and is variously estimated as 80—95 k.-cals. Thus methyl should be stable up to 1000°, in agreement with experiment. With the ethyl radical the corresponding process can occur much more easily, since an unsaturated structure is produced with the corresponding liberation of energy equivalent to the second half of the double bond : $C_2H_5 \longrightarrow C_2H_4 + H - 42$ k.-cals.

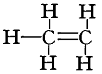
A different process occurs with the propyl and higher radicals, since now it is the weaker C–C bond which is broken. The dissociation to form methyl, $CH_3{\cdot}CH_2{\cdot}CH_2 \longrightarrow CH_3 + CH_2{:}CH_2 - 33$ k.-cals., is much easier on thermochemical grounds than is the reaction, $CH_3{\cdot}CH_2{\cdot}CH_2 \longrightarrow CH_3{\cdot}CH{:}CH_2 + H - 42$ k.-cals. The *iso*propyl radicals decompose similarly, the unsaturated molecule being formed by the simultaneous movement of a hydrogen atom during the dissociation, and as a consequence may have a slightly higher dissociation energy. For these simple radicals the order of stability is, therefore, $\mathrm{Me} > \mathrm{Et} > \mathrm{Pr^i} > \mathrm{Pr^n}$. Butyl differs from the propyl radical in that an ethyl may be formed instead of a methyl radical : $CH_3{\cdot}CH_2{\cdot}CH_2{\cdot}CH_2 \longrightarrow CH_3{\cdot}CH_2 + CH_2{:}CH_2$. In contrast with methyl, ethyl radicals and those higher in the series are stabilised by resonance. For the ethyl radical we may write structure (I), or any of the three equivalent structures (II). There are also ionic structures which are much less stable than (I) and (II) and make only a very small contribution to the resonance energy. Structure (I) is much favoured energetically and the free valency resides largely on the end carbon atom. The small probability of three structures of type (II), however, results in increased stability of the radical, and the effect increases in the series : $\mathrm{Et} < \mathrm{Pr} < \mathrm{Pr^i} < \mathrm{Bu^t}$. Table I summarises the calculated resonance energies of these radicals (Baughan, Evans, and Polanyi, *Trans. Faraday Soc.*, 1941, **37**, 377).

(I.)



$$\mathrm{H{-}\overset{H}{\underset{H}{C}}{-}\overset{H}{\underset{H}{C}}}$$

(II.)



$$\mathrm{H{-}\overset{H}{\underset{H}{C}}{=}\overset{H}{\underset{H}{C}}}$$

In view of the marked increase in radical stability in passing from CH_3 to C_2H_5, the butyl radical will decompose preferentially into C_2H_5 and ethylene. Furthermore, since the

TABLE I.

Calculated resonance energy of radicals.

Radical.	Me.	Et.	Pr^n.	Pr^i.	Bu^n.	Bu^i.	Bu^t.
No. of resonating structures ...	0	3	3	6	3	3	9
Resonance energy	0	7·1	8·6	14·1	(9·5)	10·2	21·1

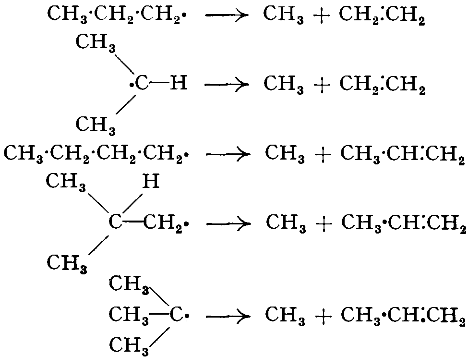
undissociated propyl and butyl radicals have approximately the same resonance stability, it follows that the butyl radical will be less stable than propyl :

$$CH_3{\cdot}CH_2{\cdot}CH_2{\cdot}CH_2 \longrightarrow CH_3 + CH_3{\cdot}CH{:}CH_2 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \qquad (3)$$

$$\longrightarrow C_2H_5 + CH_2{:}CH_2 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \qquad (4)$$

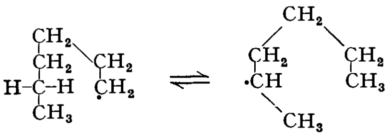
The relative rates of the alternative reactions (3) and (4) cannot be calculated directly from the energies of the processes, but it is reasonable to assume that the stabilisation in the transition state will follow that of the radical. Thus if the activation energy difference of (3) and (4) is 2 k.-cals., the rate of (4) will be three times that of (3) at 600°.

If the following dissociation reactions of the C_3- and C_4-radicals



give methyl and an unsaturated molecule are compared, it follows from the data given in Table I that the relative stabilities of the radicals in this reaction can be arranged in the following order, the stability decreasing from left to right : $Pr^n > Pr^i$; $Bu^t > Bu^i > Bu^n$.

Similar reasoning may be applied to the C_5- and higher radicals, each of which shows alternative paths of decomposition, the most probable being that determined by the relative resonance stabilisation of the initial and product radicals. As pointed out by Kossiakoff and Rice (*J. Amer. Chem. Soc.*, 1943, **65**, 590), with the long chain radical it is possible that the chain can coil round to produce a more stable isomer. For example, the following equilibrium may be established with hexyl :



The possibility also exists that the radical will shed a methyl group with the formation of a 5-membered ring.

In our previous considerations we have dealt with " saturated " radicals in which, in spite of the possibility of excited structures contributing to the stability of the normal form of the radical, the free electron resides predominantly on a single carbon atom. There is only a small chance of its being found on the hydrogens of the methyl or methylene group, but this is sufficient to modify bond energies and reactivities.

A different situation is encountered with " unsaturated " radicals, and the free valency may be shared among several atoms. Thus in the allyl radical structures (III) and (IV) are equally important :

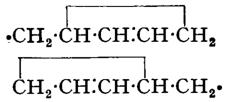
(III.) (IV.)

The free valency can now be regarded as being equally distributed between the two end carbon atoms, which will therefore be equally reactive. Similar considerations apply to other aliphatic unsaturated radicals of the general structure, $C_{2n+1}H_{2n+3}$. Thus the radical C_5H_7 will have the following five unexcited structures :

$CH_2{:}CH{\cdot}CH{:}CH{\cdot}CH_2{\cdot}$

${\cdot}CH_2{\cdot}CH{:}CH{\cdot}CH{:}CH_2$

$CH_2{:}CH{\cdot}\dot{C}H{\cdot}CH{:}CH_2$



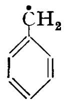
${\cdot}CH_2{\cdot}CH{\cdot}CH{:}CH{\cdot}CH_2$

$CH_2{\cdot}CH{:}CH{\cdot}CH{\cdot}CH_2{\cdot}$

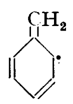
Quantum mechanical calculations (Coulson and Moffitt, *Trans. Faraday Soc.*, 1948, **44**, 81) show that the free valency is roughly evenly distributed between the odd-indexed carbon atoms with slightly greater probability for the end carbons. The free bond is zero at the even indexed carbons. This new development of the calculation of the electronic constitution of free radicals thus provides a quantitative measure of the reactivity of the different positions of the chain. The occurrence of resonance also confers a very marked stability on the radical. Thus the resonance energies of the radicals C_3H_5 and C_5H_7 discussed above are 18·7 and 30·4 k.-cals., respectively.

Much more attention has been paid to the theory of the stability of aromatic radicals, probably for two reasons : (*a*) because of the impact of the early work of Gomberg on the triphenylmethyl type radicals, and (*b*) because they constitute an ideal conjugated system much more amenable to theoretical treatment than are saturated radicals.

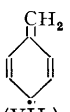
The benzyl radical may be selected as an illustration. The structures (V)—(IX) correspond to the different ways of pairing of the π electrons, the • denoting in each structure the single unpaired electron :



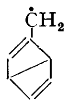
(V.)
(2 Structures)



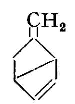
(VI.)
(2 Structures)



(VII.)



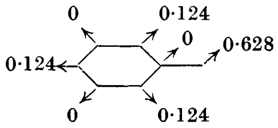
(VIII.)
(3 Structures)

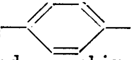


(IX.)
(2 Structures)

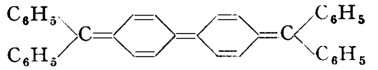
As before, the radical is considerably stabilised, and the values of the resonance energy additional to that of the parent hydrocarbon for a few simple aromatic hydrocarbons are shown in Table III (*q.v.*).

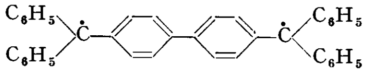
Recent theoretical developments (Coulson, Faraday Soc. Discussion, " Labile Molecules," 1947, p. 9) have also made possible the assignment of numerical values for the absolute reactivity of different positions of the molecule. The typical result for the free valency at different positions of the benzyl radical derived by the molecular orbital method is shown below :



Biradicals.—In the disproportionation reaction of both methyl and *p*-xylyl radicals considered above, methylene and ${\cdot}CH_2$——$CH_2{\cdot}$ were postulated as intermediate products. Whereas a monoradical can be defined unambiguously as possessing one unpaired electron and therefore is paramagnetic, with the above radicals the question immediately arises—are they biradicals having two unpaired electrons, or do the bonds rearrange to give molecules ? If the energy levels of the molecule and radical are sufficiently close together, then the distinction between the biradical and molecular state will not be very sharp.

The question is not new; the problem whether molecules of the Chichibabin hydrocarbon type, *e.g.*,

(X.)




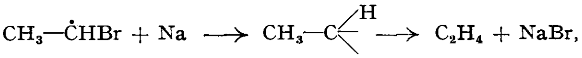
(XI.)

should be assigned a quinonoid structure (X) or a benzenoid radical structure (XI) has been frequently discussed. The question in terms of molecular-orbital theory reduces to one of the magnitude of excitation from the singlet (all electrons paired) to the triplet state (two unpaired electrons). If this value is sufficiently small, excited molecules may be present in equilibrium even at low temperature.

The energy and free valency of the molecule and biradical quinodimethane have recently been calculated by Coulson *et al.* (*loc. cit.*, p. 36), who have shown that the resonance energy of the molecule is close to that of benzene, and that the separation between the ground state and the triplet state is such that there would be a negligible concentration of radicals in equilibrium with molecules at room temperature. The free valency at the end carbon atoms is unusually high—almost the same as that of the benzyl radical—and very little lower than that of the triplet state. This explains the high reactivity at these carbon atoms. The argument, often used, that the high reactivity of large aromatic molecules implies a biradical structure can now be stated alternatively by saying that certain carbon atoms (*e.g.*, in rubrene) have a high concentration of free valency (detailed calculations on the energy of the triplet state for some 93 polyene and aromatic hydrocarbons have been made by Diatkina and Syrkin (*Acta Physicochim. U.R.S.S.*, 1946, **21**, 23).

Whereas application of the quantum theory to aromatic radicals has been particularly successful, its application to even the simplest aliphatic radicals has been somewhat disappointing. Our theoretical knowledge of methylene is not nearly so complete as that of quinodimethane and there exists a marked difference of opinion as to whether the ground state of methylene is singlet or triplet. A study of the reaction, $^-CH_2Br + Na \longrightarrow NaBr + CH_2$, which has been discussed in detail elsewhere (Bawn and Dunning, *Trans. Faraday Soc.*, 1939, **35**, 185) provides extremely strong evidence that the luminescence emitted can result only from the formation of CH_2 in a singlet state. The high reactivity claimed for methylene is not sufficient evidence to justify its existence as a free radical. In fact, kinetic studies (Bawn and Tipper, *loc. cit.*) show that CH_2 is not extremely reactive. Methylene disproportionates at 300° according to the scheme, $CH_2 + CH_2 \longrightarrow CH_4 + C$, and the activation for this reaction is 14·0 k.-cals. greater than the activation energy of the dimerisation reaction, $CH_2 + CH_2 \longrightarrow C_2H_4$. The direct association reaction with hydrogen, $CH_2 + H_2 \longrightarrow CH_4$, has an activation energy of 13·5 k.-cals.

The higher biradicals of the form $R{-}CH_2{-}CH<$ have not been identified in thermal processes. An attempt to prepare ethylidene from a saturated molecule $CH_3{\cdot}C{\begin{smallmatrix}\diagup H\\ -X\\ \diagdown X\end{smallmatrix}}$ or the radical $CH_3{\cdot}\underset{\bullet}{C}{<}^{H}_{X}$ would involve the breaking of one or both C—X bonds, and this process would be much easier if accompanied by the simultaneous formation of a double bond. Thus the reaction :

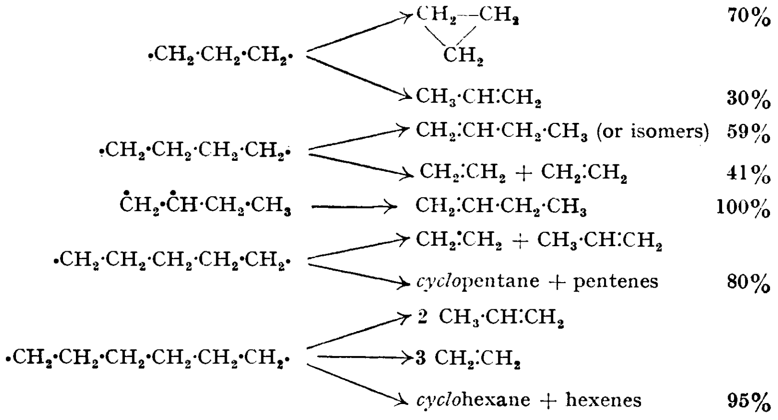


$$CH_3{-}\dot{C}HBr + Na \longrightarrow CH_3{-}C{\begin{smallmatrix}\diagup H\\ \diagdown\end{smallmatrix}} \longrightarrow C_2H_4 + NaBr,$$

when carried out in hydrogen, gives ethylene as the only product. No ethane is formed as would be expected if the ethylidene radical were formed. The direct opening of the double bond in $CH_2{\dot{:}}CHX$ with the formation of a biradical does occur in the thermal and photal initiation of polymerisation and isomerisation.

In contrast to methylene, dimethylene, and ethylidene, the higher homologues from trimethylene to hexamethylene are produced, in sodium-atom reactions, in the biradical state. With these radicals no quino-type structure exists and the possibility of the pairing of the single electrons formed at the end of a chain of methylene is extremely remote. The experimental results can be most satisfactorily explained if an intermediate and reactive biradical is formed, which undergoes either cyclisation or re-arrangement, with or without dissociation to unsaturated molecules. The analytical results at 300° are summarised in the following table.

It is interesting that there seems to be a minimum of stability in the series $[CH_2]_n$ at $n = 4$, and that this is in agreement with greater ease of formation and the stability of 5- and 6-membered rings.



Reactions of Radicals with Hydrocarbons.

So far we have been concerned only with the stability of simple radicals and with the reactions involving them alone. However, except in very special experimental circumstances, the radical is formed in the presence of other molecules which are usually in an overwhelming concentration compared with that of the radical itself; *e.g.*, in thermal reactions or in polymerisation in liquid systems, the concentration of radicals is usually 10^{-4}—10^{-9} molar. The natural tendency of the radicals to saturate themselves is the source of their marked reactivity, and this tendency is, as expected, dependent on the structure of both the radical and the reacting molecule. It is evident from the above considerations that relative probabilities of attack of an alkyl radical on a hydrocarbon would be greater at a tertiary than at a secondary, and that in turn greater than at a primary carbon atom. This is completely borne out by the direct measurements of Taylor *et al.* (*J. Chem. Physics*, 1939, **7**, 390; 1940, **8**, 396) (Tables II and III), by data on the thermal decomposition of hydrocarbons and by the chain-transfer process in polymerisation (*q.v.*). It has been shown from kinetic studies that primary < secondary < tertiary is the order of decreasing C–H bond strength. The lower activation energies with butane and *iso*butane may be ascribed to the greater reactivity of secondary and tertiary hydrogens, which in turn is due to the greater resonance stabilities of the radicals formed. The similarity of the value for ethane and *neo*pentane indicates that the removal of the primary hydrogen atom is independent of the hydrocarbon and that both of the radicals formed will have similar stability.

TABLE II.

Reaction of methyl radicals with aliphatic hydrocarbons.

Reaction.	Activation energy, k.-cals.	C–H bond strength, k.-cals.	Resonance energy of radical, k.-cals.
$CH_3 + C_2H_6$	8·3	97·5	7·1
C_3H_8	5·5	95·0	8·6
n-C_4H_{10}	5·5	94·0	(9)
iso-C_4H_{10}	4·2	86·0	10·2
*neo*Pentane	8·3	—	(7)

TABLE III.

Reaction of methyl radicals with aromatic hydrocarbons.

Reaction.	Activation energy, k.-cals.	Resonance energy of radical (β = 20 k.-cals.), k.-cals.
$CH_3 + C_6H_6$	10	0
$C_6H_5{\cdot}CH_3$	5·6	14·4
$C_6H_5{\cdot}CH_2{\cdot}C_6H_5$	5·6	26·0

The corresponding studies with aromatic hydrocarbons are not so complete, but the relatively low values for toluene and diphenylmethane (Table III) indicate side-chain attack with the formation of very stable radicals.

It follows, of course, that the greater the resonance stabilisation of a radical the less will be its tendency to capture a hydrogen from a saturated molecule. Thus, in any reaction of a radical R_1 with a hydrocarbon RH to give a new radical R, the energy change is given by :

$$R_1 + RH \longrightarrow R_1H + R$$
$$\Delta H = D_{R_1H} - D_{RH} + R_R - R_{R_1}$$

where D_{R_1H} and D_{RH} are the dissociation energies of the C–H bonds in R_1H and RH, and R_{R_1} and R_R are the resonance energies of the radicals.

It is evident that for a series of aliphatic R_1 radicals reacting with a given hydrocarbon RH the variation of activation will parallel the radical stabilities of the aliphatic radicals R_1 previously given. The reason for the preferred dimerisation of aromatic radicals such as $C_6H_5{\cdot}CH_2{\cdot}$ and $C_6H_5{\cdot}CO{\cdot}$, even in the presence of a large excess of hydrocarbon, is now understandable in view of the high resonance stability of these radicals.

Many interesting questions arise as to the attack of free radicals on unsaturated hydrocarbons. These will be taken up later and it will suffice to refer to two examples only. Both methyl and propyl radicals react very rapidly with propylene, their respective activation energies being 3·1 and 4·5 k.-cals. The corresponding reaction with ethylene is negligible and indicates that the seat of reaction is not at the double bond, but at the methyl group. This is associated with the resonance characteristics of the allyl radical formed.

$$CH_3 + CH_3{\cdot}CH{:}CH_2 \longrightarrow CH_4 + \dot{C}H_2{\cdot}CH{:}CH_2$$
$$CH_3{\cdot}CH_2{\cdot}\dot{C}H_2 + CH_3{\cdot}CH{:}CH_2 \longrightarrow CH_3{\cdot}CH_2{\cdot}CH_3 + \dot{C}H_2{\cdot}CH{:}CH_2$$

These are examples of the principle established by the work of Farmer (*Trans. Faraday Soc.*, 1942, **38**, 348) and others that the attack of free radicals on non-conjugated olefinic systems takes place at the α-methylene group. The allylic radical formed is stabilised to the extent of 18—20 k.-cals. The stabilisation is greatly increased in 1 : 3- and 1 : 4-dienes, the former of which gives the radical, $CH_2{:}CH{\cdot}CH{:}CH{\cdot}CH_2{\cdot}$, which has a resonance energy of 30 k.-cals.

Addition Polymerisation.—A most important development in free-radical chemistry has taken place in recent years in the study of vinyl polymerisations. There is no doubt whatever that thermal, photochemical, and certain types of catalysed polymerisation proceed by a free-radical mechanism. In fact the study of poly-reactions has proved to be a most useful and powerful method for the investigation of radical reactions. Some of these results will now be briefly summarised.

The fundamental reaction in the chain polymerisation is the interaction of a radical with the double bond of the polymerising monomer to give a larger free radical. This process continues until the radical is destroyed and the chain terminated.

$${\cdot}R + CH_2{:}CHX \longrightarrow R{\cdot}CH_2{\cdot}\dot{C}HX$$
$$R{\cdot}CH_2{\cdot}\dot{C}HX + CH_2{:}CHX \longrightarrow R'{\cdot}CH_2{\cdot}\dot{C}HX\text{, etc.}$$

The termination of the chain requires destruction of the growing radical. The simplest types of reaction are those by which two radicals mutually destroy each other either by combination or disproportionation :

$$R{\cdot}CH_2{\cdot}\dot{C}HX + R{\cdot}CH_2{\cdot}\dot{C}HX \longrightarrow R{\cdot}[CH_2{\cdot}CHX]_2{\cdot}R$$
$$R{\cdot}CH_2{\cdot}\dot{C}HX + R{\cdot}CH_2{\cdot}\dot{C}HX \longrightarrow R{\cdot}CH_2{\cdot}CH_2X + R{\cdot}CH{:}CHX,$$

the second process requiring hydrogen transfer.

Disproportionation is the more common reaction leading to cessation and only in one case—the OH-radical-catalysed polymerisation of methyl methacrylate (Baxendale, Evans, and Kilham, *Trans. Faraday Soc.*, 1946, **42**, 668)—has a recombination mechanism been definitely established.

The few measurements which have as yet been made of the disproportion reaction show that the chain ends have little difficulty in colliding and reacting, and that the activation energy of the process is zero or at most a few k.-cals.

The difficulty of polymerising monomers with α-methylene hydrogen atoms by a free radical mechanism is well known. Thus propylene, *iso*butene, *iso*octene, and allyl acetate give only products of low molecular weight, and this is undoubtedly due to the ready capture of an α-methylenic hydrogen atom by the polymer radical, to give the stable allylic-type radical; *e.g.*,

$$X{\cdot}CH_2{\cdot}CH{:}CH_2 + R \longrightarrow X{\cdot}CH_2{\cdot}CHR{\cdot}\dddot{C}H_2 \text{ (Initiation)}$$
$$X{\cdot}CH_2{\cdot}CHR{\cdot}\dddot{C}H_2 + X{\cdot}CH_2{\cdot}CH{:}CH_2 \longrightarrow X{\cdot}CH_2{\cdot}CHR{\cdot}CH_3 + \dddot{C}HX{\cdot}CH{:}CH_2$$

On the other hand, the typical α-methyl-containing monomers such as methacrylate or methacrylonitrile polymerise easily to high-molecular products because substitution stabilises the propagating radical and α-methylenic abstraction is greatly reduced. Similarly, the highly stable styrene-type radical, $Ph{\cdot}CH{\cdot}CH_2X$, shows little tendency to transfer. In fact, it may be concluded quite generally that substitutents effective in promoting radical stabilisation greatly reduce the probability of monomer chain-transfer.

In solution polymerisation, the solvent may also take part in transfer in a manner analogous to that of monomer transfer discussed above. The activity of the radical may be transferred to the solvent, forming a new radical which may start a fresh chain :

$$\cdot M_n + SH \longrightarrow M_n + S\cdot$$
$$\cdot S + M \longrightarrow M\cdot + HS \text{ or } SM\cdot$$

Mayo has shown (Mayo, *J. Amer. Chem. Soc.*, 1943, **65**, 2324; Gregg and Mayo, Faraday Soc. Discussion, " Labile Molecule," 1947, p. 328) that, if all the new radicals S· start chains, a simple relation exists between the average degree of polymerisation $\bar{P}$ and the chain-transfer coefficient C, viz.,

$$\frac{1}{\bar{P}} = \frac{1}{\bar{P}_0} + C\frac{[SH]}{[M]}$$

where $C = k_S/k_p$ is the ratio of the velocity constant of the reaction, $M_n\cdot + S \xrightarrow[k_S]{} M_n + S\cdot$, to that of the reaction, $M_n\cdot + M \xrightarrow[k_p]{} \dot{M}_{n+1}$, and $\bar{P}_0$ is the average degree of polymerisation in absence of the chain-transfer agent. The chain-transfer coefficient is thus a comparison of the reactivity of the growing polymer radical for reaction with the solvent and with that of the monomer. By using a variety of chain-transfer agents in the same polymeric system it is thus possible to compare the absolute velocities of reaction of a given polymer radical with a series of solvent molecules. Mayo (*loc. cit.*) has shown, from transfer measurements on the styrene radical in a series of hydrocarbons (that is, a measurement of the capacity to supply a hydrogen atom to a substituted benzyl radical), that the ease with which the hydrogen atom can be removed from a carbon atom in methane is increased appreciably by alkyl groups on the carbon atom, greatly by phenyl groups, and still more by an *o*-diphenylene group (fluorene being 1000 times more reactive than *cyclo*hexane). These results show that the increased activity in chain transfer with hydrocarbons is determined by the stability of the solvent-type radical formed, the least activation energy being required to form the most stable radical.

Copolymerisation.—When the material undergoing polymerisation consists of a mixture of two unsaturated monomers, the addition polymer formed is built up from units of each of the monomers. Such a polymer is known as a copolymer. In these mixtures the rate of polymerisation by a radical mechanism is governed by four chain-growth processes, determined by the two types of radical reacting with M_1 and M_2, *viz.* : $M_1\cdot + M_1 \xrightarrow{k_{11}} M_1\cdot$; $M_1\cdot + M_2 \xrightarrow{k_{12}} M_2\cdot$; $M_2\cdot + M_2 \xrightarrow{k_{22}} M_2\cdot$; $M_2\cdot + M_1 \xrightarrow{k_{21}} M_1\cdot$. By the use of the stationary-state method it is possible to derive the copolymerisation equation :

$$\frac{dM_1}{dM_2} = \frac{M_1}{M_2}\,\frac{r_1M_1 + M_2}{r_2M_2 + M_1}$$

where $r_1 = k_{11}/k_{12}$, and $r_2 = k_{22}/k_{21}$. The equation can be intergrated and from a knowledge of the experimentally determined monomer ratio in the polymer, together with a knowledge of the initial composition of the mixture, the reactivity ratios, r_1 and r_2, can be determined.

Now, the reactivity ratios are the ratios of the rate of addition of a monomer to a radical of its own kind and that of the rate of addition of the second monomer to the same radical. This ratio supplies, therefore, a quantitative measure of the rate of reaction of any radical with another monomer. A monomer reactivity ratio >1 indicates a tendency of the radical to perpetuate its own kind, whilst a ratio <1 indicates a preference for reaction with the other monomer. Thus the relative rate constants of the reactivity of a reference radical with a number of monomers can be determined. Table IV (Mayo, Lewis, and Walling, Faraday Soc. Discussion, " Labile

TABLE IV.

	r_1.	r_2.		r_1.	r_2.
Styrene	1·00	1·00	Vinyl chloride	17	0·02
Butadiene	0·78	—	Vinyl acetate	55	0·01
Methyl methacrylate	0·52	0·46	Vinyl ethyl ether	90	—
Methyl vinyl ketone	0·29	—	Allyl chloride	31	—
Acrylonitrile	0·40	0·04	Allyl acetate	90	0·01
2-Chloroethyl acrylate	0·54	0·10	Maleic anhydride	0·01	0·07
Methyl acrylate	0·75	0·18	Diethyl fumarate	0·30	—
Vinylidene chloride	1·85	0·14	Diethyl maleate	6·52	—
Methallyl chloride	22	—			
Methallyl acetate	71	—			

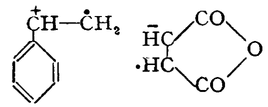
Molecule," 1947, p. 285) shows the relative reactivities of various monomers with the styrene radical. The results, for instance, show that the rate of reaction of the styrene radical with methyl methacrylate is just twice that with styrene momomer, whereas with vinylidene chloride it is about half as fast.

The table shows clearly the specific nature of the reactivity of free radicals. It so happens that the order in which radicals fall is much the same for a number of different radicals, even though the absolute rates may vary greatly from one radical to another. The broad conclusion which follows is that monomers with conjugated vinyl, phenyl, carbonyl, cyano-, or carbalkoxy-groups are considerably more reactive than the monomers without such conjugation. The data show also that the addition of one methyl or one chlorine substituent increases the reactivity of the double bond : methacrylate > acrylate; methacrylonitrile > acrylonitrile; vinylidene chloride > vinyl chloride; methallyl > allyl. It has thus become possible to compile a list (*loc. cit.*) of the ability of substituents R to increase the reactivity of the monomer $CH_2{:}CHR$ towards free radicals, viz., $C_6H_5 > H_2C{:}CH > R{\cdot}CO{\cdot} > N{:}C{\cdot} > RO{\cdot}CO{\cdot} > Br > Cl > R{:}O{\cdot} > R{\cdot}CH_2{\cdot} > H$.

It follows from our previous consideration of resonance stabilisation of radicals that the most reactive double bonds yield the most stabilised and the least reactive radicals, and that the least reactive double bonds yield the most reactive radicals.

The above order of substituents is, therefore, that corresponding to the order of their ability to promote resonance stabilisation of the methyl radical. Thus, ${\cdot}CH_2{\cdot}CH{:}CH_2$ or $CH_2{\cdot}CH_2{\cdot}C_6H_5$ should be more stabilised and less reactive than ${\cdot}CH_2Cl$ or ${\cdot}CH_2{\cdot}CH_2{\cdot}R$, and the free CH_3 should be most reactive. This order agrees with the low reactivity of triphenylmethyl and allyl radicals.

A striking feature of many free radical polymerisations is that, in many pairs, each radical reacts preferentially with the opposite-type radical, giving rise to an alternating effect in the chain. The copolymer formed consists of regularly alternating units of the two polymers, *e.g.*, styrene–maleic anhydride, and styrene–allyl acetate. Maleic anhydride or the maleic esters do not polymerise alone (or with great difficulty to low degrees of polymerisation), but will readily copolymerise with other monomers, such as styrene, and may even accelerate the rate. In many copolymerisations this tendency to alternation is superimposed upon the general activity of monomers in copolymerisation. Two explanations have been advanced to explain the alternation effect. Price (Price, *J. Polymer. Sci.*, 1946, 1 83; Price and Alfrey, *ibid.*, 1947, 2, 101) assumed that the effect arises from the difference in polarity of the radical and the double bond, a negative radical being attracted by a positive double bond and vice versa. The other explanation, due to Mayo *et al.* (*loc. cit.*), assumes that special resonance forms are available to the reactants in the transition state, *e.g.*, the double bond of the styrene molecule donates an electron to the maleic anhydride radical, the resulting structures being



The maleic anhydride portion has become a stable enolate ion, and the styrene portion has now available more resonance structures. Reactions of this type introduce a new feature which is of particular interest since electrostatic influences are not usually encountered among free radical reactions. The general effect of electron availability and the effect of substituents on the charge distribution in radicals are not yet understood and must await further experimental and theoretical developments. Nevertheless, it appears that the main features of radical reactions can be interpreted in terms of the resonance energies and the strength of bonds.