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FORMATION OF RADICALS IN REACTIONS BETWEEN VALENCY-SATURATED MOLECULES

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CONTENTS

I. Introduction 300
II. General considerations 301
III. The steric factor in bimolecular reactions involving valency-saturated molecules 302
IV. Specific systems 302
1. Reactions of molecular oxygen 302
2. Reactions of peroxides 302
3. Reactions of molecular fluorine 303
4. Reactions between organometallic compounds and alkyl halides 304

I. INTRODUCTION

It is well known that radical formation often occurs by unimolecular decomposition of various compounds with fission of the weakest bond in the molecule, e.g. by decomposition of peroxides at the O–O bond, of azo compounds at the C–N bond, of organometallic compounds at the metal–carbon bond, etc.

In recent years, evidence has accumulated in favour of the possibility of free-radical formation by a bimolecular reaction between valency-saturated molecules:

$$R'X + YR'' \rightarrow R'\cdot + XY + R''\cdot. \qquad (1)$$

In 1954, Semenov[1] published the first theoretical discussion, in a general form, of the kinetic features of reactions of this type, and arrived at the seemingly paradoxical conclusion that their activation-energy barrier should be relatively small.

This conclusion was reached on applying the principle of detailed equilibrium to certain reactions of atoms and radicals. Thus, we know[2] that the disproportionation of free ethyl radicals occurs with a very low activation energy. Hence it is a thermodynamic necessity that the reverse reaction (formation of two ethyl radicals from a molecule of ethylene and one of ethane) should also be attended by a negligible activation barrier[3], and that its activation energy should be fully accounted for by the endothermicity of the process (~ 60 kcal mole^{-1}).

A qualitative discussion of the activation energy of the reaction

$$H_2 + Cl_2 \rightarrow H\cdot + HCl + Cl\cdot, \qquad (2)$$

starting from the reverse reaction between the two atoms ($H^{\cdot}$ and $Cl^{\cdot}$) and a molecule of hydrogen chloride, leads to the same conclusion.

Arguing that a termolecular reaction between two atoms and a molecule should involve a low activation barrier, Semenov concluded that the activation energy of the bimolecular reaction (2) must be largely determined by the endothermicity of this reaction.

These ideas were confirmed in Semenov's book[1] by an approximate quantum-mechanical calculation of the activation energy of the reaction

$$H_2 + H_2 \rightarrow H\cdot + H_2 + H\cdot, \qquad (3)$$

using London's method.

The activation barrier to reaction (3), on the assumption of a linear configuration of the atoms in the transition complex, turned out to be lower than the activation energy of the reaction

$$H\cdot + H_2 \rightarrow H_2 + H\cdot.$$

Griffing's molecular orbital calculation[4,5] of the activation energy of reaction (3) confirmed that the activation barrier is small when the hydrogen atoms in the transition complex are arranged in a straight line.

In 1958 Semenov discussed[1] from a general standpoint the experimental data then available on reactions proceeding according to scheme (1) and also according to scheme (1′),

$$RX + \rangle C{=}C\langle \rightarrow R\cdot + X{-}\overset{|}{\underset{|}{C}}{-}\overset{|}{\underset{|}{C}}\cdot, \qquad (1')$$

which is a particular case of scheme (1). He showed that many baffling results could be simply explained in terms of the proposed mechanism.

By studying reactions of this type, it was possible to envisage systems in which the formation of radicals would be most likely to follow scheme (1) or scheme (1′).

Subsequent researches into reactions of this type have been carried out much more systematically, mainly at the Institute of Chemical Physics of the USSR Academy of Sciences. The present Review deals primarily with the experimental results obtained since the publication of Semenov's book[1] in 1958, with particular emphasis on kinetic investigations.

II. GENERAL CONSIDERATIONS

The reaction between two molecules R′X and R″Y with formation of two radicals according to scheme (1) is in most cases endothermic, because two covalent bonds are broken (R′–X and R″–Y) but only one new bond is formed (X–Y). If, in accordance with Semenov's views, the activation energy of reactions of this type is largely determined by the heat absorbed (in other words, if the activation barrier is small), the reaction will actually take place when D(X–Y) ≫ D(R′–X) and D(X–Y) ≫ D(R″–Y), and the heat of reaction (1), q = D(X–Y) - D(R′–X) - D(R″–Y), will not be much less than zero.

It can be shown that this condition is satisfied if the bond formed by the reaction is appreciably more polar than the two broken bonds. Thus, using Pauling's postulate of the additivity of normal covalent bond energies, we find that

$$D(R'-X) = \frac{D(R'-R') + D(X-X)}{2} + \Delta_{R'X},$$

$$D(R''-Y) = \frac{D(R''-R'') + D(Y-Y)}{2} + \Delta_{R''Y},$$

$$D(X-Y) = \frac{D(X-X) + D(Y-Y)}{2} + \Delta_{XY},$$

where $\Delta_{R'X}$, $\Delta_{R''Y}$, and Δ_{XY} are the departures from covalency of the bonds in the particular molecules.

Thus,

$$q = -\frac{D(R'-R') + D(R''-R'')}{2} + \Delta_{XY} - \Delta_{R'X} - \Delta_{R''Y} =$$

$$= -(R'-R'') + \Delta_{XY} - \Delta_{R'X} - \Delta_{R''Y} + \Delta_{R'R''}, \qquad (I)$$

where D(R′–R″) and $\Delta_{R'R''}$ are the bond energy and the departure of the bond from covalency in the molecule R′R″.

It follows from formula (I) that, if the bonds which are broken and formed in the reaction are non-polar, the heat of the reaction is equal to the energy of the R′–R″ bond, and is therefore of the order of tens of kilocalories per mole.

In order to make reaction (1) less endothermic (for a given R′–R″ bond), the departure from covalency Δ_{XY} must considerably exceed the sum $\Delta_{R'X} + \Delta_{R''Y}$. For the particular case of reaction (1)

$$X_2 + Y_2 \rightarrow X\cdot + XY + Y\cdot,$$

where the bonds in the original molecules are, of course, non-polar, formula (I) reduces to

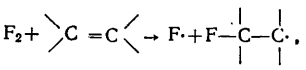
$$q = -D(X-Y) + 2\Delta_{XY}. \qquad (II)$$

We conclude from formulae (I) and (II) that a reaction of the type (1) becomes thermodynamically possible and kinetically real if one of the reactants is strongly oxidising or strongly reducing with respect to the other, so that the atom X in the resulting compound XY transfers an electron to Y (or conversely attracts an electron from the electron cloud of Y) thus making Δ_{XY} large. It follows that reaction (1) will occur in practice if it is a typical oxidation–reduction interaction. Not surprisingly, therefore, known cases of this reaction involve strong oxidising or reducing agents, e.g. oxygen, halogens, and peroxides with saturated and unsaturated hydrocarbons, peroxides with amines and sulphides, organometallic compounds with alkyl halides, etc. On the other hand, it should be noted that scheme (1) does not cover all possible cases of radical formation in redox systems[6–12].

As stated above, application of the principle of detailed equilibrium predicts an activation energy equal to the heat of reaction for strongly endothermic reactions giving rise to atoms and radicals: in other words, the activation barrier is vanishingly small. Furthermore, the theory predicts a linear configuration of the atoms in the transition complex for reactions between two H_2 molecules. This conclusion has been confirmed by quantum-mechanical calculations[1,4].

When extending these conclusions to other systems of more practical importance, we should not expect a linear

activated complex in all cases. Thus, a non-linear structure will probably be more favourable if not only s electrons are involved in the formation of bonds in the transition complex. For example, in the reaction between olefins and halogens



the most favourable configuration of the transition complex is probably one in which the F–F and C–C bonds are mutually almost perpendicular.

Not even the conclusion of a zero activation barrier can be assumed to apply unequivocally to all real systems. Thus, although the overall activation energy E (including the heat of reaction q) decreases on going from strongly exothermic towards thermally neutral processes, there is no reason to suppose that E tends to zero for thermally neutral reactions, i.e. that when $q = 0$ the activation barrier $\epsilon = E - q$ is zero.

The approximate Polanyi–Semenov relation[1]

$$\varepsilon = A - \alpha q, \qquad \text{(III)}$$

is known to hold for free-radical reactions: in other words, ϵ is a maximum for $q = 0$.

Semenov has given evidence[1] showing that expression (III) is generally applicable to the kinetics of elementary reactions and is by no means confined to reactions between radicals and molecules. When the transition complex has a complicated structure, the quantity A, which depends on many factors, such as bond elongation, distortion of valence angles, etc., does not remain constant even in series of related reactions. This introduces a deviation from linearity in the relation between ϵ and q.

The reactions represented by scheme (1) are similar to radical reactions in the simplicity of structure of the transition complex, since in both cases the valence angles are not significantly distorted on formation of the transition complex. We can therefore expect expression (III) to hold, with constant values of A and α, in series of related reactions of this type. Thus, the activation barrier will evidently not be zero, and will be a maximum for thermally neutral reactions.

III. THE STERIC FACTOR IN BIMOLECULAR REACTIONS INVOLVING VALENCY-SATURATED MOLECULES

Table 1 lists the preexponential factors of a number of reactions, calculated by the transition state method. In most cases, the transition complex was assumed to have a linear configuration. As was to be expected, the steric factor P is in many cases much less than unity. For the relatively simple molecules considered in Table 1, and for reactions between a diatomic molecule and a complicated molecule, P lies in the range 10^{-1}–10^{-5}.

TABLE 1.

Reaction	$10^{-11}A$, $cm^3\ s^{-1}$
$H_2+C_2H_4 \rightarrow H+C_2H_5$	3.32 [74]
$H_2+H_2 \rightarrow H\cdots H\cdots H \rightarrow H+H_2+H$	4670
$F_2+H_2 \rightarrow F\cdots F\cdots H\cdots H \rightarrow F+HF+H$	530
$F_2+HBr \rightarrow F\cdots F\cdots H\cdots Br \rightarrow F+HF+Br$	7.80
$F_2+HI \rightarrow F\cdots F\cdots H\cdots I \rightarrow F+HF+I$	6.26

IV. SPECIFIC SYSTEMS

1. Reactions of Molecular Oxygen

The bimolecular reaction

$$RH + O_2 \rightarrow R\cdot + HO_2\cdot, \qquad (4)$$

is a well-known example of initiation of oxidation, and of some other chain reactions[1,13].

Nalbandyan and his coworkers[14] have recently studied this reaction in the particular case of acetaldehyde. They found that hydrogen peroxide is a primary product of the molecular reaction, which suggests the mechanism

$$CH_3C(=O)H + O_2 \rightarrow CH_3\dot{C}O + HO_2\cdot, \qquad (5)$$
$$HO_2\cdot + CH_3COH \rightarrow H_2O_2 + CH_3\dot{C}O.$$

In agreement with earlier data[15,16], the activation energy of the reaction was found to be 30 kcal $mole^{-1}$, which is not very different from the heat of reaction (5).

Extending Semenov's approach to liquid-phase oxidation, Denisov showed[17–19] that free radicals can be formed in the termolecular reaction between RH and oxygen

$$RH + O_2 + HR \rightarrow R\cdot + H_2O_2 + R\cdot.$$

When $D(R–H) < 90$ kcal $mole^{-1}$ the termolecular reaction is less endothermic than the bimolecular reaction (4). Assuming that the activation energy was fully accounted for by the heat of reaction, Denisov concluded that at high hydrocarbon concentrations (10 M) the termolecular reaction should be faster than the bimolecular reaction for hydrocarbons and other compounds having a bond energy $D(R–H) < 90$ kcal $mole^{-1}$.

Experimental results for a number of compounds have confirmed the formation of radicals by a termolecular mechanism[18–21]. These results, and those of other authors, are summarised in a review[19] and in a monograph[13].

2. Reactions of Peroxides

The decomposition of the hydroperoxides formed as intermediates in oxidations is a reaction of the type known as "degenerate chain branching". It is now realised that, in addition to the unimolecular decomposition ROOH → → RO· + ·OH, the bimolecular reactions of hydroperoxide molecules with the following species are very important sources of free radicals

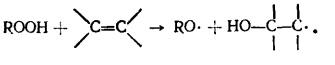
(a) another molecule of the hydroperoxide[22]

$$2\,ROOH \rightarrow RO\cdot + H_2O + ROO\cdot.$$

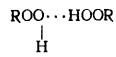
(b) a solvent molecule[1,23,24]

$$ROOH + R'H \rightarrow RO\cdot + H_2O + R'\cdot.$$

(c) a molecule of an unsaturated compound[19]



A hydrogen-bonded intermediate association complex[22] could be a precursor in the bimolecular interaction of two hydroperoxide molecules:



We can envisage two extreme cases, leading to entirely different reaction kinetics. If the equilibrium lies far over towards the monomeric hydroperoxide molecules, it is easy to see that both the kinetic equation and the reaction rate will be indistinguishable from those corresponding to the bimolecular reaction between two hydroperoxide molecules. In other cases, the concentration of the association complex may be the predominant factor, and in this case the reaction will occur through this complex and follow first-order kinetics.

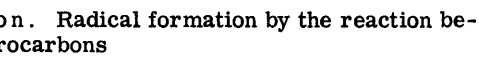
More detailed experimental results on the formation of radicals from hydroperoxides can be found in the reviews mentioned above[13,19].

3. Reactions of Molecular Fluorine

(*a*) Initiation. Radical formation by the reaction between F_2 and hydrocarbons



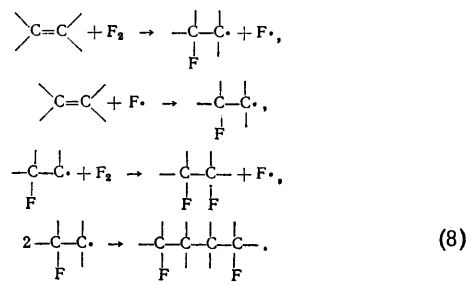
(6)



(7)

is particularly favourable thermodynamically, because all reactions of these two types are either practically athermic or exothermic. Miller[25-27], as long ago as 1956, pointed out that these reactions have to be included in the fluorination scheme in order to explain the reaction products, particularly in the case of olefins.

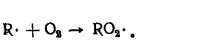
As a result of his study of the fluorination products of olefins over a range of temperatures, Miller proposes the following scheme for the reaction between F_2 and olefins[28]



(8)

The high rate of formation of radicals explains the relatively high yield (tens per cent) of the dimeric product in reaction (8).

A direct confirmation of the formation of radicals during the reaction between F_2 and olefins was obtained by Kapralova and Shilov[29], who studied these reactions by the electron spin resonance method. They found that, when fluorine is passed over an olefin frozen at the temperature of liquid nitrogen, free radicals are formed on the surface. These radicals were shown to be peroxidic and to result from the interaction of the primary radicals with oxygen, present as an impurity in the fluorine:

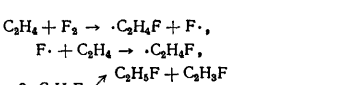


According to their rate of reaction with fluorine when frozen at 77°K, ethylene and its derivatives can be arranged in the sequence[30]



The first three members of the series react too fast for accurate measurement even at liquid nitrogen temperature. The temperature at which these reactions take place indicates that the activation energy must be low: the experimental value for the reaction between F_2 and C_2HCl_3 is close to 0.5 kcal mole^{-1}

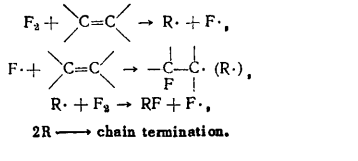
The elementary reaction between fluorine and ethylene has been investigated in the gas phase by the low-pressure flame method[30,31]. The conditions (very large excess of ethylene) are chosen so as to exclude secondary chain propagation reactions ($R^{\cdot} + F_2 \rightarrow RF + F^{\cdot}$) when the rate constant of the primary reaction between F_2 and C_2H_4 is large. The products of the reaction were identified as C_2H_3F, C_2H_5F, and $C_4H_8F_2$, corresponding to the mechanism



(9)

The absence of $C_2H_4F_2$ among the reaction products shows that chain propagation is effectively excluded under the chosen conditions. The rate constant of reaction (9) is $8 \times 10^{14} \exp(-4600/RT)$ cm^3 s^{-1}.

Rodgers[32,33] studied the kinetics of the slow gas-phase reactions of fluorine with 2,3-dichlorohexafluorobut-2-ene and with perfluorobut-2-ene. His kinetic results are consistent with the following chain mechanism for the fluorination:



(7)

From the overall activation energy for the reaction Rodgers, estimated the activation energy for reaction (7), assuming values close to zero for the other reactions. The activation energy of the chain generation reaction was found to be quite large — 16 kcal mole^{-1} for perfluorobutene and 23–25 kcal mole^{-1} for dichlorohexafluorobutene.

Thus, the activation energy of reactions of type (7) is not zero, even for ethylene, whose reaction is exothermic by 16 kcal. When electronegative substituents are introduced into the olefin molecule, the activation energy increases for surface and gas-phase reactions alike. This may be partly caused by a decrease in the enthalpy change accompanying the elementary reaction of fluorine with the olefins, but the available experimental data do not allow us to establish a quantitative relationship. There is a substantial difference in activation energy between the gas-phase reactions of fluorine and the surface reactions, the latter having the lower value of ϵ. This is evidently a manifestation of the specificity of surface reactions, in which the resulting free radical remains bound to the surface.

Very much less is known about elementary reactions of fluorine of the type

$$RH + F_2 \rightarrow R\cdot + HF + F\cdot,$$

The only reaction of this type which has been the object of a kinetic study is the reaction

$$F_2 + HI \rightarrow F\cdot + FH + I\cdot, \quad (10)$$

This reaction was investigated by the low-pressure flame method[30]: the measured activation energy was 3.5 kcal mole^{-1}. However, it is possible that the authors failed to exclude the chain reaction completely, and that the true activation energy is somewhat higher.

Reaction (10) is unique in the value of its heat of reaction. In other cases, e.g.

$$F_2 + H_2 \rightarrow F\cdot + FH + H\cdot, \quad (11)$$

$$F_2 + HCl \rightarrow F\cdot + FH + Cl\cdot, \quad (12)$$

$$F_2 + CH_4 \rightarrow F\cdot + FH + CH_3\cdot, \quad (13)$$

$$F_2 + C_4H_{10} \rightarrow F\cdot + FH + C_4H_9\cdot, \quad (14)$$

the thermal effect is much smaller. The rate constants and activation energies of these reactions are not known. Several workers[30,34-36] have shown that under certain conditions the fluorination of hydrogen, hydrogen chloride, methane, and butane is very slow or even undetectable at room temperature or above. Under different conditions the fluorination of those same compounds is known to proceed explosively by a spontaneous thermal or chain reaction[37]. A high reaction rate is not sufficient proof that the elementary reactions (11)–(14) occur readily, since the rate of initiation may not play an essential role. On the other hand, the fact that under certain conditions the fluorination is immeasurably slow proves that the rate constant of the elementary reactions (11)–(14) is small and that their activation energy is large.

Published experimental results[30,34-36] in conjunction with the data of Table 1 enable us to estimate a lower limit for the activation energy of these reactions: the value thus obtained is ~ 15–20 kcal mole^{-1}. In fact, the activation energy can, of course, be as much higher as we wish. This is evidence for the existence of a considerable activation barrier in practically athermic reactions of fluorine, proceeding according to scheme (6).

(*b*) Chain Branching. We have already pointed out that the bimolecular reaction of hydroperoxides with various compounds can provide a chain-branching mechanism in chain reactions in which hydroperoxides are formed as intermediates. Reaction (4) can also act as a branching process if RH is an intermediate product and the bond energy D(R–H) is much lower than in the original compound. Branching of this type occurs, for example, in the high-temperature oxidation of methane. In this case the branching product is formaldehyde, which reacts with O_2 according to scheme (4). From the point of view of reaction mechanism, this so-called "degenerate" branching is indistinguishable from initiation. Thus, a degenerate branching reaction is either a unimolecular decomposition or a bimolecular reaction involving a molecule of an intermediate product which is chemically more reactive than the starting compound.

Somewhat similar ideas have been developed[37] in recent years for the non-degenerate branching mechanism, which causes spontaneous ignition by a chain reaction. It has been shown[38-40] that the reactions of molecular fluorine involve a branching chain mechanism, the branching of the chains being realised by chemical reactions of intermediate species.

The difference from degenerate branching resides in the fact that the intermediate species react in an excited state, for which the excitation energy is supplied by exothermic chain development reactions. Thus, the concentration of these intermediate species does not follow the Maxwell–Boltzmann energy distribution. The life of the excited particles, limited by energy dissipation by collisions, is short and of the same order as the time of chain development. If the particle is able to react during this time with formation of atoms or radicals, chain branching occurs. The branching can proceed either as a unimolecular decomposition at the weakest bond or as a bimolecular chemical reaction between excited particles and the initial molecules.

The chain branching which occurs during fluorination of hydrogen[40] is an example of a bimolecular branching reaction. It has been shown that this reaction has definite pressure limits, separating a region of extremely slow reaction from a region of spontaneous ignition. In view of the relative simplicity of the system $H_2 + F_2$, we can unambiguously identify the chain development mechanism as analogous to the Nernst chain in chlorination:

$$F\cdot + H_2 \rightarrow HF + H\cdot,$$

$$H\cdot + F_2 \rightarrow HF + F\cdot + 98 \text{ kcal}.$$

Kapralova and her coworkers[38,40] have suggested that branching results from the chemical reaction of an excited molecule with a starting molecule:

$$F_2 + HF^* \rightarrow F\cdots F\cdots H\cdots F \rightarrow F\cdot + FH + F\cdot. \quad (15)$$

It may be noted that this reaction leads formally to the same result as energy transfer from an excited HF* molecule to a molecule of fluorine:

$$HF^* + F_2 \rightarrow HF + F_2^*,$$

$$F^*_2 \rightarrow 2F\cdot.$$

This type of branching mechanism by energy transfer was proposed by Semenov at a very early stage in the development of the theory of branched chain reactions[41,42], and has since been invoked by various workers[44-46]. However, it is in the chemical reaction that the most effective utilisation of large amounts of energy can be expected[37,43]. Hence, the bimolecular interaction mechanism of scheme (1) can be applied to this system, too.

According to the experimental results, reaction (15) has a much lower probability than dissipation of the energy. However, because of the very long chains in the fluorination of hydrogen, the probability is sufficient to cause non-stationary reaction and spontaneous ignition. The same mechanism can be applied to the fluorination of methane and other compounds, when the resulting molecule does not contain a sufficient amount of energy for unimolecular decomposition at the weakest bond.

Clearly, however, the more complex the resulting molecule, the less probable is bimolecular reaction with F_2, because the probability of energy concentration at the site of attack decreases[37].

4. Reactions between Organometallic Compounds and Alkyl Halides

We have considered some examples of strong oxidising agents reacting according to Semenov's scheme. We shall

now discuss the reactions of organometallic compounds, which are known to be strong reducing agents. When metal alkyls react with halogen derivatives according to scheme (1)

$$R'Hal + MR'' \rightarrow R'\cdot + MHal + \cdot R'', \qquad (16)$$

the considerable energy of the resulting ionic bond M–Hal largely balances the rupture of the relatively weak M–R″ bond and of the R′–Hal bond, so that the heat required by the elementary reaction (16) and its activation energy should both be small. Reactions between alkyl halides and organometallic compounds occur in the familiar Wurtz, Fittig, and Grignard reactions. Although the mechanism of these reactions has been studied in detail in comparatively few cases, the available information shows that the mechanism can vary according to the nature of the metal, the reactants, and the medium. Metals with a low ionisation potential (e.g. potassium) form relatively polar M–C bonds, and this gives the reaction a heterolytic character, particularly in polar solvents. On changing to metals with a high ionisation potential the polarity of the M–C bond decreases, and this, as has been shown above, favours the formation of free radicals, particularly in non-polar hydrocarbon media.

Among the alkali metals, lithium has the highest ionisation potential[47], and therefore the Li–C bond is more covalent than the Na–C and K–C bonds. Thus, free-radical formation is most likely to be found in the reactions of lithium alkyls with alkyl halides.

The free-radical mechanism of the reaction of organometallic compounds with halogen derivatives has been discussed on a number of occasions[48–53].

Bryce-Smith[54] obtained a direct proof of the formation of radicals in his work on the reactions of the metals Li, Na, K, and also butyllithium, butylsodium, butylpotassium, with butyl iodide, bromide, and chloride in the presence of cumene, which reacts with free radicals to give 2,3-dimethyl-2,3-diphenylbutane:

$$R\cdot + C_6H_5CH(CH_3)_2 \rightarrow RH + C_6H_5\dot{C}(CH_3)_2,$$
$$2\,C_6H_5\dot{C}(CH_3)_2 \rightarrow C_6H_5C(CH_3)_2C(CH_3)_2C_6H_5.$$

An appreciable amount of the dimethyldiphenylbutane is formed only in the reactions of lithium and butyllithium with butyl halides. In the reactions of sodium, potassium, butylsodium, and butylpotassium its formation was negligible. Bryce-Smith proposed the following reaction scheme:

$$C_4H_9I + 2M \rightarrow C_4H_9M + MI,$$
$$C_4H_9I + C_4H_9M \rightarrow 2\,\dot{C}_4H_9 + MI,$$
$$2\,C_4H_9 \begin{cases} \rightarrow C_8H_{18} \\ \rightarrow C_4H_{10} + C_4H_8 \end{cases},$$
$$C_4H_9 + HS \rightarrow C_4H_{10} + \dot{S},$$
$$\left.\begin{aligned} C_4H_9M + C_4H_9I &\rightarrow C_8H_{18} + MI \\ C_4H_9M + C_4H_9I &\rightarrow C_4H_8 + C_4H_{10} + MI \end{aligned}\right\} \text{ionic path.}$$

Bryce-Smith stresses that free-radical formation is very probable when the colliding molecules take up a linear configuration R...Li...X...R, so that the alkyl groups are as remote from each other as possible. Formation of free radicals was demonstrated in a similar way by Okhlobystin and his coworkers[55], who studied the reaction of organomagnesium compounds with alkyl halides in hydrocarbon solvents. In their work on the reaction between butylmagnesium iodide and butyl iodide and chloride in cumene, they detected the formation of the dimethyldiphenylbutane, together with butane and butene, among the reaction products. They explained their results by the scheme

$$C_4H_9MgI + C_4H_9I \rightarrow 2\,\dot{C}_4H_9 + MgI_2,$$
$$2\,C_4H_9 \rightarrow C_4H_8 + C_4H_{10},$$
$$C_4H_9 + C_6H_5CH(CH_3)_2 \rightarrow C_4H_{10} + C_6H_5\dot{C}(CH_3)_2,$$
$$2\,C_6H_5\dot{C}(CH_3)_2 \rightarrow C_6H_5C(CH_3)_2C(CH_3)_2C_6H_5.$$

The mechanism of the reaction is substantially changed on passing to a polar solvent[56–58]. Thus, the reaction RMgX + R′X in ethers yields mainly RR′, apparently without formation of free radicals. When the reaction is carried out in tetrahydrofuran and dimethoxyethane, alkyl exchange is observed[57]: $RMgX + R'X \rightleftharpoons R'MgX + RX$.

In general, therefore, scheme (1) by no means exhausts the mechanism of the interaction of organometallic compounds with halogen-containing molecules. Thus, the large and important class of reactions between the transition-metal halides and aluminium alkyls does not usually involve radicals as intermediates[59,60], although schemes similar to (1) have frequently been postulated[61].

The mechanism of these reactions, leading to well-known polymerisation catalysts, falls outside the scope of the present Review.

The kinetics and mechanism of the reactions between ethyllithium and a number of alkyl halides have been investigated[62–67] at the Institute of Chemical Physics of the USSR Academy of Sciences. The formation of free radicals was most unequivocally demonstrated in the reaction between ethyllithium and triphenylchloromethane[62]. The relatively low rate of recombination of triphenylmethyl radicals[68] contributed to their formation in concentrations sufficient to enable the reaction to be studied by electron spin resonance. It was found that the concentration of $(C_6H_5)_3C^{\cdot}$ radicals passes through a clearly defined maximum immediately after the reactants are mixed, and then drops to an equilibrium value.

The initial formation of a concentration of radicals in excess of equilibrium proves that these radicals are a primary product in the reaction:

$$(C_6H_5)_3CCl + LiC_2H_5 \rightarrow (C_6H_5)_3C\cdot + LiCl + \cdot C_2H_5. \qquad (17)$$

Kinetic investigation led D'yachkovskii and his coworkers[62] to conclude that the activation energy of reaction (17) is 4–5 kcal mole^{-1}. These workers studied the fate of the ethyl radicals, and concluded that they are formed as complexes with C_2H_5Li molecules: this makes their reactivity quite different from that of free ethyl radicals.

Similar conclusions were reached from a study[63] of the mechanism of the reaction between ethyllithium and ethyl iodide in hydrocarbon solvents. The experimental results — formation of ethane, ethylene, and butane in the reaction, formation of C_2H_5D if the reaction is carried out in deuterated solvents, and decrease in the yield of ethane in the presence of free-radical acceptors — confirm the formation of free ethyl radicals during the reaction. At the same time, a quantitative estimate of the yield of C_2H_5D and certain other facts show that only a fraction of the $C_2H_5^{\cdot}$ radicals are free: the remainder appear to be bound in a complex with ethyllithium. The explanation of this result is evidently to be found in the fact that ethyllithium is present in solution, and reacts with a molecule of alkyl halide, in the form of associated complexes[69–73]. Hence, when a C_2H_5 radical is formed from

a C_2H_5Li molecule, it is already bound to molecules of ethyllithium which form the complex.

The stability of the bond between a C_2H_5 radical and the C_2H_5Li molecules is still unknown, but it is evident that the reactivity of a radical which is bound in this way must be considerably lower than the reactivity of a free $\cdot C_2H_5$ radical formed from a C_2H_5I molecule.

Our work on the kinetics of the reactions of C_2H_5Li with ethyl iodide, bromide, and chloride, and with some other organic chlorides[66,67], has led us to conclude that the rate-determining stage is the first elementary act

$$(C_2H_5Li)_n\, C_2H_5Li + IC_2H_5 \rightarrow \cdot C_2H_5\,(C_2H_5Li)_n + LiI + \cdot C_2H_5.$$

The most important kinetic results are summarised in Table 2. The most obvious conclusion from the data for different chlorides is that the reaction rate decreases and the activation energy increases as the energy of the C–Cl bond increases.

As D(R–Cl) is varied from 48 to 80 kcal mole^{-1}, the rate constant for the reaction at 90° decreases by a factor of approximately 10^5. The variation of the activation energy E with D(R–Cl) is not far from linear. Since the heat of reaction q is almost completely determined, in the reactions of different chlorides with ethyllithium, by differences in the C–Cl bond energy, the linear dependence of E_{act} on D(R–Cl) implies that E_{act} must be linearly related to q, i.e. that the Polanyi–Semenov rule is obeyed.

The numerical values of the coefficients A and α in the expression $\epsilon = A - \alpha q$ could be estimated only approximately, because of uncertainty in the value of D(Li–C_2H_5) in solution. Adopting the value obtained for the gas phase[75] without allowance for molecular association, the variation of ϵ with q was described by the formula $\epsilon = 13 - 0.33q$. It is interesting to note that the values of A and α obtained in this way are not very different from the corresponding values for radical reactions.

The reactions of ethyllithium with ethyl iodide, bromide, and chloride were examined to establish the effect of the nature of the halogen on the rate of reactions of this type. In this series, the increase in the energy of the C–Hal bond is accompanied by a corresponding increase in the energy of the Li–Hal bond, so that the heats of these reactions remain approximately constant:

	D(C–Hal) (Ref. 47), kcal mole^{-1}	D(Li–Hal) (Ref. 47), kcal mole^{-1}	q, kcal mole^{-1}
C_2H_5I	51	83,6	13.4
C_2H_5Br	65	100	12.5
C_2H_5Cl	80	112,5	13.5

At the same time, the activation energy of the reaction increases considerably from C_2H_5I to C_2H_5Cl, varying linearly with the energy of the C–Hal bond. Similar changes in activation energy are observed in many series of reactions of different types, in which the energy changes associated with the rupture and with the formation of bonds are mutually compensating, so that the thermal effect does not change appreciably. Typical of these are the reactions between atomic sodium and alkyl halides[76,77], the reactions between the CF_3 radical and methyl chloride, bromide, and iodide[78], the unimolecular decomposition of alkyl halides[79,80] by the scheme $C_2H_5Hal \rightarrow C_2H_4 + HHal$, and others[81].

Thus, this type of behaviour would appear to be common to the kinetics of elementary reactions. It can be formulated in the following way: if, in a series of related reactions, the heat of reaction is approximately constant because the change in the energy of the bond undergoing fission is compensated by the corresponding change in the energy of the bond which is formed, then the activation barrier opposing the reaction increases with increase in the energy of the bonds involved in the reaction.

TABLE 2.

Reaction	log A	E, kcal × mole^{-1}	D(C–Hal) (Ref. 47), kcal mole^{-1}	20+log k_{90}
$C_2H_5Li+C_2H_5I$	6.74	13.6	51	3.561
$C_2H_5Li+C_2H_5Br$	7.08	16.3	65	2.286
$C_2H_5Li+C_2H_5Cl$	7.00*	19.0*	80	0.590
$C_2H_5Li+C_4H_9Cl$	6.97	18.8	76	0.673
$C_2H_5Li+iso\text{-}C_3H_7Cl$	7.00*	17.6*	74	1.400
$C_2H_5Li+t\text{-}C_4H_9Cl$	7.00*	13.7*	70	3.750
$C_2H_5Li+C_6H_5CH_2Cl$	4.55	10.5	61	3.225
$C_2H_5Li+C_6H_5Cl$	7.59	14.1	59	4.087
$C_2H_5Li+(C_6H_5)_2CCl$	4.32	5.0	48	5.853

* The value log A = 7.00 was assumed, and E was calculated on this assumption.

This rule has been explained[67] in terms of the increase in the steepness of the potential energy curves on passing to more stable bonds.

The existence of the relationship $\Delta E = \beta \Delta D$ points to some connection between the values of A for series of similar reactions in which the condition $\epsilon = A - \alpha q$ is obeyed, e.g. for the series of reactions between C_2H_5Li and chlorides, bromides, and iodides.

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U.D.C. 541.54:541.124.7

CHAIN TRANSFER WITH FISSION

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CONTENTS

1. Introduction 308

2. Kinetic and thermodynamic features of chain transfer with fission (CTF) 309