U. D. C. 547.218

Homolytic Substitution at the Metal Atom in Organometallic Compounds

E.B.Milovskaya

Homolytic substitution at the metal atom involves a wide range of organic derivatives of non-transition metals and takes place in reactions with free radicals where the reaction centre is located at an oxygen, nitrogen, or sulphur atom. The qualitative and quantitative aspects of these reactions have been examined. The applicability of the relations established both in the treatment of a series of reactions involving organometallic compounds and for synthetic purposes has been demonstrated. The bibliography includes 75 references.

CONTENTS

I. Introduction 384
II. Homolytic substitution at the metal atom 384
III. Analysis of certain reactions involving organometallic compounds 389

I. INTRODUCTION

Oxidation reactions of organic derivatives of non-transition metals have been attracting attention for a long time. These reactions are not only of theoretical but also of practical interest. In particular, the oxidation of metal alkyls leads to a convenient method of synthesising oxygen-containing compounds which are difficult to obtain otherwise; combinations of the metal alkyl-oxygen type are sometimes capable of initiating the radical polymerisation of vinyl monomers at a low temperature, etc.

The oxidation of metal alkyls takes place very rapidly, in a fraction of a minute, and since the process is heterogeneous the use of kinetic criteria to infer its mechanism proved to be difficult. Moreover, it has been established that inhibitors of free-radical reactions (hydroquinone, diphenylamine, etc.) do not affect this process. Therefore it has been suggested that the oxidation has a polar and not a homolytic mechanism. However, some authors admit the possibility of homolytic stages in the oxidation process†.

In connection with the discovery of powerful inhibitors of free-radical processes, methods for the synthesis of pure stereoisomeric forms of metal alkyls, and the application of ESR spectroscopy, in recent years it was possible to discover stages in the oxidation process which had been unknown hitherto. It was shown that the oxidation of organic derivative of boron, zinc, cadmium, aluminium, magnesium, antimony, and bismuth constitutes a bimolecular homolytic substitution at the metal atom via a mechanism of the type which obtains in S_H2 reactions‡.

In the case of polyvalent organometallic compounds, reactions of the S_H2 type proceed not only with peroxy- but also with alkoxy- and acyl radicals and with radicals in which the reaction centre is located at a nitrogen or sulphur atom.

This review deals with qualitative and quantitative aspects of the homolytic substitution reactions. Certain processes involving organometallic compounds have been analysed and it has been shown that the relations discovered may be used for preparative purposes in organic chemistry.

†The oxidation reactions and subsequent reactions of organometallic peroxides have been considered in reviews [1–3].

‡The term S_H2 reactions was introduced by Pryor [4] and was used by Davies in relation to bimolecular reactions of free radicals with the metal atom in organometallic compounds.

II. HOMOLYTIC SUBSTITUTION AT THE METAL ATOM

1. Oxidation of Organic Derivatives of the Elements

The beginning of a fundamental and systematic revision of earlier views concerning the nature of the oxidation of organic derivatives of the elements must be attributed to a study of the oxidation of 1-phenylethylboronic acid (1967), where a complete loss of stereospecificity was observed in the hydroperoxide obtained as a result of the reaction [5]. It was established that the kinetics of the oxidation of organic derivatives of boron, zinc, cadmium, aluminium, antimony, and bismuth are influenced by inhibitors of free-radical processes: galvinoxyl, nitroxide phenothiazine. An induction period, the duration of which depends on the inhibitor concentration and the nature of the metallic compound, is observed in their presence; free-radical sensitising agents (copper salts and hyponitrite) initiate the process [6–9]. The existence of a radical stage in the oxidation of organomagnesium compounds is indicated by the loss of stereospecificity and the formation of a mixture of the *exo*- and *endo*-forms of norbornylmagnesium halides having a unique composition [10].

On the basis of literature data [5,6,8–10], Davies and coworkers formulated the hypothesis that the oxidation of organometallic compounds, like the oxidation of hydrocarbons, is a radical chain process the stages of which are presented below:

$$\text{sensitisation} \xrightarrow{\text{slow}} \text{radicals}, \quad (1)$$

$$R^{\cdot} + O_2 \xrightarrow{\text{very rapid}} RO_2^{\cdot}, \quad (2)$$

$$RO_2^{\cdot} + R_nM \xrightarrow[k_p]{\text{slow}} RO_2MR_{n-1} + R^{\cdot}, \text{ chain propagation}, \quad (3)$$

$$2RO_2^{\cdot} \xrightarrow[k_{обр.}]{} \text{inactive products, chain termination}. \quad (4)$$

The mechanism shows that the stage determining the rate of propagation is the interaction between peroxy-radicals and the organometallic component [reaction (3)], alkyl radicals behaving as reaction chain transferring agents. Chain termination involves bimolecular interaction

between two peroxy-radicals leading to inactive products. The sensitisation stage will be considered below§.

Organoboron compounds are very useful for the investigation of such reactions. The bond between boron and carbon is purely covalent [14], which favours homolytic processes. In contrast to organic derivatives of aluminium or zinc, there is a wider set of stable boron alkyls available, which gives rise to a greater scope for the investigation of the oxidation reaction in this class of compounds.

A detailed kinetic study of the oxidation of a wide range of organoboron compounds yielded the quantitative characteristics of the chain propagation stage and made it possible to establish a relation between this stage and the structure of the initial boron alkyl [15,16]. It has been shown for oxydiboron derivatives, boroxins, and mono- and di-alkoxy-derivatives of boron, which are oxidised at a moderate rate, that the process is described by the relation

$$-\frac{d[O_2]}{dt} = k[BR_3]R_i^{1/2},$$

where $k = k_p/(2k_t)^{1/2}$ and R_i is the rate of sensitisation. The relation follows from Eqns. (1)–(4).

Table 1. Rate constant ratios $k_p/(2k_t)^{1/2}$ in the autoxidation of organoboron compounds [15,16] (iso-octane, 30°C).

Compound	$k_p/(2k_t)^{1/2}$, litre$^{1/2}$ mole$^{-1/2}$ s$^{-1/2}$				
	R=*n*-Bu	s-Bu	t-Bu	1-phenylethyl	benzyl
$(RBO)_3$	0.21	40	870	850	64
R_3BOR	4.4	11	—	—	—
R_3BOBR_2	43	56	—	—	—
R_3B[a]	300[b]	70[c]	—	—	300[d]

[a] In pyridine–octane mixture.
[b] $K_{eq} = 2.2 \times 10^2$ litre mole^{-1}.
[c] $K_{eq} = 0.16$ litre mole^{-1}.
[d] $K_{eq} = 8.7 \times 10^3$ litre mole^{-1}.

In a kinetic study of the oxidation of n-butyl-, s-butyl, benzyl-, and phenyl-boron derivatives, which react very rapidly, pyridine (Py), which is a powerful complex-forming agent, was introduced into the mixture. The relation established in this case is of the form

$$-\frac{d[O_2]}{dt} = k\frac{[BR_3]}{[Py]}\left(\frac{R_i}{2k_t}\right)^{1/2},$$

where $k = k_p/K_{eq}$ and reflects the following complex formation reaction:

$$BR_3 + Py \overset{K_{eq}}{\rightleftharpoons} BR_3 \cdot Py.$$

§This view has been expressed also in studies by other investigators [7,11,12]. Davies and coworkers previously held different views on the oxidation mechanism; at present this school has made the greatest experimental contribution and has obtained most of the quantitative characteristics of the mechanism described by Eqns. (1)–(4); see also Davies and Roberts [13].

This reaction results in a decrease of the initial concentration of the boron alkyl; only the non-complexed form of the alkyl is involved in the oxidation reaction. The ratios $k_p/(2k_t)^{1/2}$, i.e. the quantities corresponding to the "oxidisability" of the organoboron compounds, and the propagation rate constants are listed in Tables 1 and 2.

Table 2. Rate constants for chain propagation in the autoxidation of boron alkyls [15,16] (iso-octane), 30°C.

Compound	k_p, litre mole^{-1} s^{-1}				
	R=*n*-Bu	s-Bu	t-Bu	1-phenylethyl	benzyl
$(RBO)_3$	$1 \cdot 10^3$	$5 \cdot 10^4$	$3 \cdot 10^4$	$4 \cdot 10^6$	$1 \cdot 10^6$
R_3BOR	$3 \cdot 10^4$	$1 \cdot 10^4$	—	—	—
R_3BOBR_2	$3 \cdot 10^5$	$7 \cdot 10^4$	—	—	—
R_3B	$2 \cdot 10^6$	$8 \cdot 10^4$	—	—	$5 \cdot 10^6$
$2k_t$(ROO)	$4 \cdot 10^7$	$1.5 \cdot 10^6$	$1 \cdot 10^3$	$2.5 \cdot 10^7$	$3 \cdot 10^8$

Evidently the "oxidisability" is determined by the nature of the substituting groups; groups containing oxygen retard the oxidation, which has been attributed to an increase of electron density at boron due to oxygen: $B-OR \leftrightarrow \bar{B}=\dot{O}R$. The chain propagation rate constant does not depend quite so explicitly on the nature of the R groups.

Table 3. Rate constants for the abstraction of a hydrogen atom from organic compounds by peroxy-radicals [15].

Compound	k, litre mole^{-1} s^{-1}	°C	Compound	k, litre mole^{-1} s^{-1}	°C
Toluene	0.24	30	Phenol	$4.3 \cdot 10^3$	65
Cumene	0.18	30	2,6-di-t-butyl-4-methoxyphenol	$8 \cdot 10^4$	65
Tetralin	6.4	30	Diphenylamine	$4 \cdot 10^4$	65
Cyclohexa-1,4-diene	$1.5 \cdot 10^3$	30	*NN'*-Diphenyl-*p*-phenyldiamine	$1.9 \cdot 10^6$	65

While the ratio $k_p/(2k_t)^{1/2}$ decreases in the series n-butylboron < s-butylboron < t-butylboron, this type of relation is not observed for the chain propagation rate constant. Hence it follows that the differences between the oxidisabilities of the compounds are related mainly to changes in the chain termination rate constant¶. The relation between k_p and the nature of R is fairly complicated and reflects a number of effects which frequently act in opposition (the stability of the radical removed, the steric accessibility of the boron atom, the reactivity of the attacking radical, etc.). Table 2 shows that the rate constant for homolytic substitution at the boron atom is extremely high, particularly when compared with the abstraction of a hydrogen atom by a peroxy-radical (Table 3). Thus dealkylation of the polyvalent boron atom

¶The kinetic relations show that the chain termination is in all cases a consequence of the interaction between peroxy-radicals.

by peroxy-radicals is one of the most rapid organic reactions of the S_H2 type. The sensitisation stage is particularly complicated in self-sensitised reactions. Davies and coworkers suggest that there are three processes responsible for the formation of radicals, namely direct oxidation, which is important at the very beginning of the process, monomolecular decomposition of the peroxide formed, and finally bimolecular interaction between the oxidised and non-oxidised forms of the boron alkyl [Eqns. (5) to (7)].

$$R_3B + O_2 \xrightarrow{k_5} R_2BO_2^{\cdot} + R^{\cdot}, \quad (5)$$

$$R_3B + O_2 \rightarrow [R_2BOOR] \rightarrow [R_2BO^{\cdot} + {}^{\cdot}OR] \begin{cases} \xrightarrow[k_6]{\text{liberation from cage}} \\ \xrightarrow{\text{reaction in cage}} [R(RO)BO^{\cdot} + R^{\cdot}] \rightarrow \end{cases} \quad (6)$$

$$\xrightarrow{\text{recombination}} R(RO)_2B, \cdot$$

$$R_2BOOR \rightarrow \begin{bmatrix} R_2BO \ldots OR \\ \uparrow \quad \downarrow \\ R \ldots BR_2 \end{bmatrix} \begin{cases} \xrightarrow{\text{liberation from cage}} R^{\cdot} + R_2BO^{\cdot} + R_2BOR \\ \xrightarrow{\text{recombination in cage}} 2R_2BOR. \end{cases} \quad (7)$$

The numerical values of the rate constants for the primary sensitisation steps (k_5) and for the monomolecular decomposition of certain peroxyboron compounds (k_6) are listed in Table 4.

Table 4. Rate constants for the primary sensitisation (k_5) and monomolecular decomposition of the peroxide (k_6).

Compound	$10^3 k_5$, litre mole^{-1} s^{-1} (benzene, 25°C) (Ref.17)
R_3B	R = iso-Bu, s-Bu, cyclohexyl 0.9 1.9 21.9
R_2BOOR	$10^4 k_6$, s^{-1} (octane, 30°C) (Ref.15)
	R = n-Bu, s-Bu 0.11 3.8

Apart from Davies, investigators who studied the polarisation of methyl methacrylate (MMA) under the influence of systems based on $BR_3 + O_2$ also pointed to reaction (7) as a source of free radicals [3,18,19]. This view is confirmed by kinetic results obtained under model conditions [11,12,15,20]. At the same time, it has been noted [15] that the experimental data at present available concerning the pathways involved in the formation of free radicals are still inadequate for final conclusions.

2. Reaction of RO· Radicals with the Metal Atom in Organometallic Compounds

The interaction of alkoxy-radicals with the central metal atom is an example of a non-chain radical substitution process. The existence of such reactions was demonstrated for the first time and then investigated by Krusic and Kochi [21] and by Davies and coworkers [22–24] using a low-temperature ESR technique (from −100°C onwards). The experiments were performed directly in the spectrometer tube containing the organometallic compound; the free alkoxy-radicals were obtained by the photolysis (P) or thermolysis (T) of t-butyl peroxide or di-t-butyl hyponitrile.

Although one might have expected under these conditions signals corresponding to the formation of products resulting from the abstraction of a hydrogen atom by RO· radicals from the solvent or from the alkyl group of the organometallic compound, analysis of the spectra showed that radicals of only one type are generated, mainly those which were incorporated previously in the metal alkyl molecule (Table 5). The results indicate the occurrence of a quite unique reaction of the RO· radical with the C–metal bond [Eqn. (8)], which had not been observed hitherto:

$$RO^{\cdot} + R_xM \rightarrow (ROMR_x)^{\cdot} \rightarrow ROMR_{x-1} + R^{\cdot}. \quad (8)$$

Table 5. The nature of the radicals formed in the interaction between RO· and MR [22,24].

MR	Method of decomposition of peroxide	Solvent	Radical detected by ESR
$ZnEt_2$	P	Tetrahydrofuran	Et
$CdMe_2$	T	Iso-octane	Me
B-n-Bu_3	P, T	"	n-Bu
B-s-Bu_3	P	t-Butyl peroxide	s-Bu
$AlMe_3$	P	Iso-octane	Me
$AlEt_3$	P	"	Et
Et_2AlOBu	P	"	Et
$SbEt_3$	P	"	Et
$BiEt_3$	T	t-Butyl peroxide	Et

It is not clear whether reaction (8) is a stepwise or synchronous S_H2 process, i.e. whether $(ROMR_X)^{\cdot}$ is a true intermediate complex or a transition stage [24]. The postulate that the reaction pathway (8) is preferable to the abstraction of hydrogen atoms is based on the greater energy gain. This follows from a comparison of the stabilities of the corresponding dissociated and formed bonds; some of the available literature data are presented in Table 6.

Table 6. Comparison of the heats of reaction ΔH between RO· and MR and between RO· and $-\overset{|}{\underset{|}{C}}-H$.

Type of bond in M–R	Bond strength, kcal mole^{-1}		ΔH	References
	M–C	M–O		
B–C	85	125	20	25,24
	70	110	40	26
Al–C	65	138	70	25,27
H–C	99	H–O 111	12	28

The energy gain in this pathway for aluminium alkyls is so great that there is actually no need for an initial decomposition of the peroxide into free radicals [22]†; we shall consider later the mechanism of this interaction.

†After this fact had been established, Davies employed in a later study a monoalkoxyaluminium derivative.

The importance of the energy parameter has been demonstrated for trialkoxyboron; in this case, the only pathway is one involving the abstraction of a hydrogen atom from the alkoxy-group with formation of the $(RO)_2B\dot{O}CHCH_3$ radical[21]. The absolute values of the homolytic substitution rate constants and the activation energies for this process have been established for a series of boron alkyls[24]. The required parameters were obtained by the method of competitive reactions in which t-BuO· radicals were able to react with BR_3 and with cyclopentane (C_5H_{10}):

$$(R'O)_2 \xrightarrow{P} 2R'O\cdot \begin{cases} \xrightarrow[k_9]{BR_3} R'OBR_2 + R\cdot & (9) \\ \xrightarrow[k_{10}]{C_5H_{10}} R'OH + C_5H_9\cdot . & (10) \end{cases}$$

(R'=t-Bu)

The concentrations of alkyl and cyclopentyl radicals were determined by ESR and k_9 was evaluated from the expression

$$\frac{k_9}{k_{10}} = \frac{[C_5H_{10}][R\cdot]}{[BR_3][C_5H_9\cdot]}$$

using the literature value of k_{10}. The relevant data (the rate constants k_9 and the activation energies E_9) are presented in Table 7.

The excited triplet form of a carbonyl compound frequently behaves like a free radical in the hydrogen abstraction reaction[4]. It has been shown[29,30] that the excited form of a carbonyl compound, like an alkoxy-radical, gives rise to homolytic substitution of the boron alkyl:

$$Me_2CO \xrightarrow{P} Me_2CO^*,$$
$$Me_2CO^* + BR_3 \xrightarrow{k_{11}} Me_2\dot{C}OBR_2 + R\cdot . \qquad (11)$$

Table 7. Absolute rate constants and activation energies for the S_H2 reaction between $(CH_3)_3CO\cdot$ radicals and boron alkyls[24] (iso-octane, 30°C).

Compound	k_9, litre mole^{-1} s^{-1}	E_9, kcal mole^{-1}
n-Bu_3B	$3\cdot10^7$	0
iso-Bu_3B	$1\cdot10^6$	1.1
s-Bu_3B	$3\cdot10^5$	4.5
$(n\text{-BuBO})_3$	$6\cdot10^5$	2.2
$(iso\text{-BuBO})_3$	$1\cdot10^6$	2.3
$(s\text{-BuBO})_3$	$6\cdot10^5$	—
$(t\text{-BuBO})_3$	$3\cdot10^6$	2.6
C_5H_{10}	k_{10} $2\cdot10^5$	E_{10} 5.2

In conformity with Eqn. (11), two signals were detected in the ESR spectra[30]. The data for the rate of the S_H2 reaction of acetone in the triplet state (Table 8) show that its reactivity in relation to boron alkyls is comparable to that of t-BuO· radicals and varies in the same sequence (cf. Table 7).

3. Interaction of Organometallic Compounds with Acyl Radicals

The interactions of organic derivatives of tin, lead, and mercury, with a number of acyl peroxides and perbenzoates, which have been investigated by Razuvaev and coworkers[31-34], are logically closely related to the reactions discussed in the preceding sections. It has been established that the interaction occurs only at the decomposition temperature of the peroxide; the products indicate the simultaneous occurrence of several processes. One of these is homolytic substitution at the metal atom by free acyl radicals formed as a result of the decomposition of the peroxide.

Table 8. Rate constants for the S_H2 reaction between acetone in the triplet state and boron alkyls at 20°C.[30]

Compound	k_{11}, litre mole^{-1} s^{-1}
Pr_3B	$1.4\cdot10^7$
$(C_6H_{13})_3B$	$8\cdot10^6$
n-Bu_3B	$7\cdot10^6$
iso-Bu_3B	$8\cdot10^4$
s-Bu_3B	$<10^4$

Organic derivatives of aluminium, thallium, and cadmium constitute a special group[35-41]. Their interaction with acyl peroxides is so vigorous that there is no necessity for a preliminary decomposition of the peroxide into free acyl radicals for homolytic substitution‡.

The interaction of AlR_3 (R = ethyl or isobutyl) with benzoyl peroxide (BP), which has been investigated in detail[35-37] both in the absence and presence of a free-radical acceptor, established a number of characteristic features of the process. The reaction is of the donor–acceptor type and is almost instantaneous down to −70°C; the stoichiometric ratio is Al:BP = 2:1. The final products are compounds corresponding to the reactions of free alkyl radicals and dialkylaluminium benzoate; only one Al–C is involved in the reaction and the yield of free radicals is about 10%. For the associated and non-associated forms of the aluminium alkyl, the reaction proceeds identically and is not accompanied by the formation of free benzoate radicals:

$$2AlR_3 + (PhCOO)_2 \rightarrow \left[\begin{array}{cc} R_2Al & AlR_2 \\ \vdots & \vdots \\ O & O \\ | & | \\ PhC \cdots O{-}O \cdots CPh \end{array} \right] \rightarrow \qquad (12)$$

$$\rightarrow 2R_2AlOCOPh + 2R'\rightarrow RH,\ R_{-H},\ R{-}R.$$

The $AlEt_3$–BP interaction takes place virtually with zero activation energy and the rate constant k for the decomposition of the peroxide exceeds by many powers of 10 the rate constant for its thermal decomposition ($k \simeq 10^{-2}$ at 0°C)[42,43].

A kinetic study of the interaction between $AlEt_3$ and BP in the presence of an electron donor–ethyl acetate (EA)—showed that the rate of formation of free radicals follows the relation

$$V = k\frac{[Al]}{[EA]}[BP]^{0.5}, \text{ where } k = \frac{k_{in}}{K_{eq}},$$

‡Strictly speaking, these are trimolecular and not bimolecular reactions.

where $k = k_{in}/K_{eq}$, which corresponds to the reactions formulated below:

$$\begin{gathered} AlEt_3 + EA \overset{K_{eq}}{\rightleftharpoons} AlEt_3 \cdot EA, \\ 2AlEt_3 + BP \overset{k_1}{\rightleftharpoons} [(AlEt_3)_2 \cdot BP] \overset{k_2}{\rightleftharpoons} 2\,(Et_3AlOCOPh)^{\cdot} \rightarrow \\ \xrightarrow[\text{slow}]{k'_{in.}} 2Et_2AlOCOPh + 2Et; \quad k_{in} = k'_{in.}(k_1k_2)^{0.5}. \end{gathered} \tag{13}$$

Thus the results show that only the non-complexed form of the metal alkyl takes part in the reaction with benzoyl peroxide and the role of the electron donor reduces to the decrease of its initial concentration. As shown above, similar relations have been established also for the interaction of peroxy-radicals with R_3B in the presence of an electron donor [15,16]§.

The results obtained for triethylthallium [38,41] and diethylcadmium [40] suggest that mechanism (12) is general for this group of organometallic compounds. The driving force of the interaction is due to the enormous energy gain resulting from a number of causes: the formation of the complex leads to a weakening of the pre-existing bonds, which facilitates their dissociation, while, on the other hand, the final result of the reaction is related to the conversion of the covalent M–C bond into the ionic M–O–C–R linkage. Using $AlEt_3$–BP as an example, one may attempt to calculate the thermal balance for this interaction. By analogy with the heat of formation of a complex of $AlEt_3$ with an ester [42–44], in the formation of the complex via the two carbonyl groups of the peroxide approximately 20 kcal mole^{-1} is presumably evolved. The decomposition of the peroxide is known to require 30 kcal mole^{-1}, i.e. in the complex this process takes place almost without the consumption of heat. The stability of the AlOCOR linkage has been calculated from the formula $E = e^2/R$. If one assumes that the charge $e = 4.8 \times 10^{-10}$ e.s.u. and the distance between the charges $R = 2$ Å, [47,48] then $E \simeq 160$ kcal mole^{-1}¶. The dissociation energy of the Al–C bond (65 kcal mole^{-1}) [25] yields an overall energy gain of about 100 kcal mole^{-1}.

As already mentioned, when t-butyl peroxide interacts with $AlEt_3$, an extremely vigorous reaction also takes place [22]. The mechanism of this process is analogous to that discussed for benzoyl peroxide [Eqn. (12)]. In this case, the final product is an alkoxy-derivative of aluminium [39].

Thus homolytic substitution at the metal atom is determined by the energy gain in the conversion of M – C into M–O or M–OCOR bonds, the Lewis acidity of the metal alkyl, and the ease of dissociation of the peroxide bond. The first condition is to some extent correlated with the position of the metal in the electronegativity series, being reflected in the amount of ionic character of the bond formed. For example, boron alkyls, which contain the least "metallic" of the elements of the series considered, altogether fail to react with benzoyl peroxide [49].

§The conclusion that only the non-complexed form of $AlEt_3$ is involved in the reaction with benzoyl peroxide follows from the data obtained in a study of the kinetics of the polymerisation of vinyl chloride under the influence of the $AlEt_3$–BP system in the presence of electron donors: butyl ether, pyridine, and allyl acetate [44]. However, it has been suggested [45] that the interaction between triethylaluminium-ether and peroxides involves the displacement of one ligand by another.

¶Infrared spectra show that the Al–OCOR bond formed is ionic according to its vibration frequency [35].

4. Interaction of Metal Alkyls with Radicals having the Reaction Centre at the Nitrogen Atom

The reactions of free radicals with the reaction centre at the nitrogen atom have been investigated for the interaction of organic derivatives of boron and antimony with the dimethylnitrogen radical generated photolytically or thermally from tetramethyltetrazene [50]. Data indicating the occurrence of the following reactions have been obtained by ESR and ^{1}H NMR spectroscopy:

$$\begin{gathered} [(CH_3)_2N{-}N{=}]_2 \xrightarrow{P} \underset{(I)}{2\,(CH_3)_2N^{\cdot}} + N_2, \\ (I) + MR_x \rightarrow (CH_3)_2N{-}MR_{x-1} + R^{\cdot}. \end{gathered} \tag{14}$$

The rate constant for reaction (14) involving Bu_3B is 8×10^3 litre mole^{-1} s^{-1} at 35 °C. A similar reaction takes place with aluminium alkyls, giving a high yield of the final product, which is of preparative value for the synthesis of aluminium amides [51]. The ESR spectra for the reaction of aluminium alkyls with $(CH_3)_2N^{\cdot}$ are less definite than for alkoxy-radicals [50]. The reactions of succinimidyl radicals with organic derivatives of tin have been investigated; in the case of alkyl derivatives, the process proceeds via a radical mechanism [52]. It has been shown [53] that the interaction of R_3SnH with triazenes $Ar\underset{1}{-}N\underset{2}{=}N\underset{3}{-}N(R')-R''$ can proceed via different pathways depending on the nature of R′ and R″: either via an $S_H2(\alpha)$ reaction with formation of $R_3SnNR'R''$ or via an $S_H2(\gamma)$ 1–3 displacement reaction leading to $Ar{-}\underset{\displaystyle SnR_3}{\underset{|}{N}}{-}N{=}NR''$ and R′.

The reactions discussed in Section II, subsections 2, 3, and 4 are radical non-chain processes, i.e. a significant concentration of free radicals could be achieved in this way. For this reason, they may serve as a very convenient secondary source of free alkyl radicals with a wide variety of structures.

5. Reactions of Metal Alkyls with Radicals having the Reaction Centre at the Metal Atom

Reactions equivalent to those discussed for oxygen- and nitrogen-containing radicals obtain also with radicals where the reaction centre is at the sulphur atom. The interaction between thiophen and organic derivatives of antimony and bismuth has been investigated; thiyl radicals were generated with the aid of hyponitrile and the process was followed by NMR spectroscopy [54]. The possibility of sensitising this reaction with the aid of free radicals and of inhibiting it with phenothiazine or galvinoxyl suggested [54] that a free-radical chain process takes place, the stages of which are presented below:

$$R^{\cdot} + C_6H_5SH \rightarrow RH + \underset{(II)}{C_6H_5S^{\cdot}}, \tag{15}$$

$$(II) + MR_3 \rightarrow C_6H_5S{-}MR_2 + R^{\cdot}. \tag{16}$$

The formation of alkyl radicals following attack by sulphur-containing radicals has been demonstrated under the conditions of the photolysis of diaryl or dialkyl sulphides in the presence of boron alkyls in the tube of the ESR spectrometer [55]. The relative rates of the S_H2 reaction with participation of the organoboron compound and the reaction involving the addition of butane-1-thiol to an olefin [55] have been investigated by the method of competing reactions. The following reactivity series has been established for boron alkyls: n-Bu_3B > iso-Bu_3B > > s-Bu_3B. According to the authors, the rate of the

dealkylation reaction is determined by the steric characteristics of the butyl group. The rate constants have the same order of magnitude as for the reaction of alkoxy- or peroxy-radicals with BR_3 (10^5–10^7 litre mole^{-1} s^{-1}). The energy gain in this process is due to the difference between the stabilities of the B–S and B–C bonds, amounting to approximately 10 kcal mole^{-1}.

6. Homolytic Substitution at the Metal Atom in the Reaction with Alkyl Radicals

Homolytic substitution at the metal atom is not limited to reactions with radicals having the reaction centre at the heteroatom. Thus the kinetic parameters of the interaction of methyl radicals (produced by the photolysis of azomethane in the gas phase) with BEt_3 have been estimated [56]. The relations obtained for the two possible pathways of the process [Eqns. (17) and (18)] suggest that in this case the homolytic substitution reaction is slightly preferable to the abstraction of hydrogen:

$$CH_3^{\cdot} + BEt_3 \begin{cases} \xrightarrow{k_{17}} Et^{\cdot} + CH_3BEt_2; & k_{17}=10.6-\frac{5200}{4.58T}, \quad (17) \\ \xrightarrow{k_{18}} CH_4 + CH_3\dot{C}HBEt_2; & k_{18}=12.6-\frac{7780}{4.58T}. \quad (18) \end{cases}$$

Probably the reaction of $AlEt_3$ (or $AlEt_2Cl$ with azobisisobutyronitrile (under the conditions of the decomposition of the latter) can be classified as homolytic substitution at the metal atom by an alkyl radical; signals due to two radicals–the ethyl and dimethylcyanomethyl radicals—were detected in the ESR spectra [57].

The data presented show that reactions involving homolytic substitution at the metal atom are characteristic of a wide range of organometallic compounds. The energy gain in these reactions ensures the formation of significantly more stable bonds than those existing previously; the reactions take place with a low activation energy at a high rate, which is in many cases close to the rate determined by diffusion. Consequently, such reactions can successfully compete with other free-radical processes.

III. ANALYSIS OF CERTAIN REACTIONS INVOLVING ORGANOMETALLIC COMPOUNDS

1. Radical Polymerisation

We shall consider certain examples the interpretation of which has become possible (or more definite) on the basis of the relations discussed above. Mixtures of metal alkyls with oxygen are used as low-temperature sensitising systems, but the mechanism of the formation of free radicals under these conditions has hitherto remained fairly tentative. The reactions discussed in the first part of the review [Eqns. (5)–(7)], responsible for the formation of free radicals on oxidation, take place during the sensitisation of polymerisation under the influence of such systems. The relative contribution of reactions (5)–(7) to sensitisation is related to the nature of the metal alkyl, the relative concentrations of oxygen and the metal alkyl, temperature, etc. [2,3]

In a study of the polymerisation of methyl methacrylate in the presence of boron alkyl, it was noted that inhibitors do not affect the process. This suggested an unusual mechanism of chain propagation, involving a complex of the growing radical with the boron alkyl, which is not acted upon by the inhibitor [58,59]. It has been shown that this idea [60–62] is erroneous and the causes of the above effect have been discussed. Firstly, Arimoto [58] employed inhibitors which are in general ineffective in the polymerisation of methyl methacrylate (hydroquinone, *N*-phenyl-α-naphthylamine, etc.). The second reason is related to the specific features of the action of the usual inhibitors on boron alkyls. This phenomenon must be considered in detail, since it reflects features which are fundamentally different from those usually adopted in the chemistry of radical reactions. The interaction of inhibitors with free alkyl radicals generated in the sensitisation stage leads to the appearance of radicals with the reaction centre at oxygen or nitrogen atoms. As stated above (Section II, subsections 2 and 4), in model conditions, the reaction of radicals having such a structure with boron alkyls involves an extremely high energy gain. This leads to the formation of a new highly active alkyl radical and not a stable radical from the inhibitor. For polymerisation (M = monomer) using an inhibitor, for example quinone $C_6H_4O_2$, this is illustrated by the following mechanism [61,62]:

$$M_xM^{\cdot} + C_6H_4O_2 \rightarrow \underset{(III)}{M_xMOC_6H_4O^{\cdot}}, \quad (19)$$

$$(III) + BEt_3 \rightarrow M_xMOC_6H_4OBEt_2 + Et^{\cdot}, \quad (20)$$

$$Et^{\cdot} + M \rightarrow EtM^{\cdot}, \quad (21)$$

$$\text{etc}\dagger.$$

Thus, in a radical process involving boron alkyls (oxidation or sensitisation of polymerisation), the usual inhibitors behave at best as chain transfer agents.

All the data quoted demonstrate that only stable free radicals such as galvinoxyl or compounds generating such radicals as a result of the primary reaction (phenothiazine, nitroxide) can serve as effective inhibitors of processes involving organometallic compounds.

One may quote further examples concerning polymerisation and demonstrating that homolytic substitution at the metal atom alters the primary pattern of radical reactions. It has been established that aluminium alkyls are involved in the thermal polymerisation of styrene (St), behaving as highly active chain-transfer agents ($C_{transf} \simeq 20$) [64]. This process does not occur as a result of the abstraction of a hydrogen atom from the alkyl group but as a homolytic substitution of the entire group which had been previously linked to aluminium:

$$\text{poly-St}^{\cdot} + AlR_3 \rightarrow \text{poly-StAl}R_2 + R^{\cdot}. \quad (22)$$

Thus, instead of the relatively inactive benzyl radical, reaction (22) generates a highly active alkyl radical. Presumably the energy gain in such a reaction is associated with the stabilisation of the Al–benzyl bond relative to the Al–alkyl bond as a result of electron transfer from the benzene ring.

In the polymerisation of methyl methacrylate under the influence of systems of the type AlR_3–BP, the organoaluminium component is an extremely active chain-transfer agent [65]. Probably in this case the energetically favourable reaction between the oxygen form of the growing PMMA$^{\cdot}$ radical,

$$\sim CH_2-\underset{\underset{H_3C}{|}}{\overset{\overset{\cdot}{C}}{|}}-\underset{\underset{OR}{|}}{C}=O \leftrightarrow \sim CH_2-\underset{\underset{H_3C}{|}}{C}=\underset{\underset{OR}{|}}{C}-\dot{O},$$

†The possibility of employing a metal alkyl–hydroquinone (or quinone) mixture for the sensitisation of radical polymerisation, is also related to reactions of type (19)–(21). [63]

and the aluminium alkyl, leading to the termination of the material chain, is responsible for the observed effect.

It is well known that aluminium alkyls are themselves incapable of sensitising the polymerisation of vinyl monomers. However, when a very high concentration of $AlEt_3$ and illumination are employed, the radical polymerisation of methyl methacrylate proceeds very effectively[66]. The mechanism of the formation of free radicals is in this case probably very similar to that of reactions between the excited form of the carbonyl compound and the boron alkyl [Eqn. (11)].

2. The Applications of Reactions involving Homolytic Substitution of Groups Linked to the Metal in Synthetic Organic Chemistry

In this subsection we shall confine ourselves to a small number of examples in order to demonstrate the possibilities inherent in the process involving homolytic substitution of groups linked to the metal in preparative organic chemistry. Controlled oxidation of organoboron compounds has been used by Brown and coworkers to synthesise a wide variety of compounds. The process has a free-radical mechanism and includes a series of consecutive reactions at the boron atom with participation of $R_2^{\cdot}$, $RO^{\cdot}$, and $RS^{\cdot}$ radicals [67-73,75].

Conditions for the quantitative oxidation of organoboron compounds to the corresponding alcohols have been found [67]. It has been stated that the reaction is appreciably inhibited by a small amount of iodine [68]. The oxidation of Bu_3B in the presence of organic iodides R'I' (R' = benzyl, allyl, *p*-nitrobenzyl, etc.) leads to the formation of butyl iodide in an amount equivalent to that of the initial iodide and of the recombination products of the R'' radicals [69]. Reactions responsible for the observed course of the process have been suggested:

$$R_3B + O_2 \rightarrow R_2BO_2^{\cdot} + R^{\cdot}, \quad (23)$$

$$R^{\cdot} + R'I \rightarrow RI + R''^{\cdot}, \quad (24)$$

$$2R''^{\cdot} \rightarrow R'-R', \quad (25)$$

$$R''^{\cdot} + O_2 \rightarrow R'O_2^{\cdot}, \quad (26)$$

$$R'O_2^{\cdot} + R_3B \rightarrow R'O_2BR_2 + R^{\cdot}. \quad (27)$$

$\alpha\beta$-Unsaturated aldehydes or ketones with an external double bond are known to undergo a 1,4-addition reaction with boron alkyls, giving rise to saturated carbonyl derivatives [70]. The process is inhibited by galvinoxyl radicals. This led to the assertion that it has a homolytic mechanism; earlier it was believed that the reaction has a polar mechanism with a six-membered transition state [71]. In the absence of specially introduced sensitisers, unsaturated β-substituted carbonyl compounds are incapable of this type of reaction with boron alkyls. The presence of a measurable amount of oxygen (or of other free-radical sensitisers) ensures the development of the process in the required direction and the yield of the desired product is close to theoretical. The intermediate stages of this reaction (for methyl propenyl ketone) are quoted below [72]:

$$BR_3 + O_2 \rightarrow R^{\cdot}, \quad (28)$$

$$R^{\cdot} + CH_3CH{=}CH{-}CO{-}CH_3 \rightarrow \underset{\underset{\underset{R}{|}}{CH_3CH{-}\dot{C}H{-}CO{-}CH_3}}{\underset{\updownarrow}{\underset{\underset{R}{|}}{CH_3CH{-}CH{=}C\dot{O}{-}CH_3}}}, \quad (29)$$

(IV)

$$(IV) + BR_3 \rightarrow \underset{\underset{\underset{R}{|}}{CH_3CH{-}CH{=}CO{-}BR_2}}{\underset{\text{hydrolysis}\;\downarrow}{\underset{\underset{R}{|}}{CH_3CH{-}CH_2{-}C{=}O}}} + R^{\cdot}, \quad (30)$$

(31)

The synthesis of homologues of the tetra-atomic carbon chain, achieved by the interaction of the monoepoxy-derivative of buta-1,3-diene with the boron alkyl, is closely related to these reactions [reactions (28)–(31)]. [73]

It has been established that the reaction of organic derivatives of boron with mercaptans hardly occurs in the absence of oxygen or peroxy-compounds. In the presence of free-radical sensitising agents, the process proceeds at a high rate and leads to the formation of dialkylthioboronic acids and saturated hydrocarbons [74]. A convenient synthesis of organic sulphides from disulphides and boron alkyls has been proposed by Brown and Midland [75].

---o0o---

The review can be aptly concluded by Davies' words [13]: "Reactions of the bimolecular homolytic substitution type take place readily at a metallic centre, particularly where the displaced group is an alkyl radical. This provides a new context for investigating the behaviour of free radicals, and is the key to the understanding of many organometallic reactions".

REFERENCES

1. G. Sosnowsky and Y. Braun, Chem. Rev., 66, 529 (1966).
2. T. G. Brilkina and V. A. Shushunov, Uspekhi Khim., 35, 1431 (1966) [Russ. Chem. Rev., No. 8 (1966)].
3. E. B. Milovskaya, L. V. Zamoiskaya, and E. L. Kopp, Uspekhi Khim., 38, 928 (1969) [Russ. Chem. Rev., No. 5 (1969)].
4. W. A. Pryor, "Free Radicals" (Translated into Russian), Atomizdat, Moscow, 1970.
5. A. Davies and B. Roberts, J. Chem. Soc. (B), 17 (1967).
6. A. Davies and B. Roberts, J. Chem. Soc. (B), 311 (1969).
7. P. Allies and P. Brindley, J. Chem. Soc. (B), 1126 (1969).
8. A. Davies and B. Roberts, J. Chem. Soc. (B), 1074 (1968).
9. A. Davies and S. Hook, J. Chem. Soc. (C), 1660 (1971).
10. A. Davies and B. Roberts, J. Chem. Soc. (B), 317 (1969).
11. K. Ingold, Chem. Comm., 911 (1969).
12. J. Grotewold, J. Hernandez, and E. Lissi, J. Chem. Soc. (B), 182 (1971).
13. A. Davies and B. Roberts, Nature, Phys. Sci., 229, 221 (1971).
14. L. Pauling, "The Nature of the Chemical Bond" (Translated into Russian), Goskhimizdat, Moscow–Leningrad, 1947.
15. A. Davies, K. Ingold, B. Roberts, and R. Tudor, J. Chem. Soc. (B), 698 (1971).
16. S. Korcek, G. Watts, and K. Ingold, J. Chem. Soc. Perkins Trans. II, 243 (1972).
17. P. Brindley and J. Hodson, Chem. Comm., 202 (1972).
18. C. Bawn et al., J. Chem. Soc., 397 (1959).
19. R. Hansen, J. Polymer Sci., A2, 4215 (1964).

20. R. Hansen and R. Hamann, J. Phys. Chem., 67, 2868 (1963).
21. P. Krusic and J. Kochi, J. Amer. Chem. Soc., 91, 3942 (1969).
22. A. Davies and B. Roberts, Chem. Comm., 699 (1969).
23. A. Davies and B. Roberts, J. Organometall. Chem., 19, 17 (1969).
24. A. Davies, D. Griller, and B. Roberts, J. Chem. Soc. (B), 1823 (1971).
25. T. Mortimer, "Reaction Heats and Bond Strengths" (Translated into Russian), Izd. Mir, Moscow, 1964, p. 190.
26. T. Charnley, H. Skinner, and N. Smith, J. Chem. Soc., 2282 (1952).
27. J. Hay, P. Hopper, and J. Robb, J. Organometall. Chem., 28, 193 (1971).
28. F. A. Cotton and G. Wilkinson, "Advanced Inorganic Chemistry: A Comprehensive Text" (Translated into Russian), Izd. Mir., Moscow, 1969, Part I, p. 121.
29. M. Engina and E. Lissi, J. Organometall. Chem., 29, 21 (1971).
30. A. Davies, B. Roberts, and J. Scaiano, J. Chem. Soc. (B), 2171 (1971).
31. G. A. Razuvaev, M. S. Vyazankin, and O. S. D'yachkovskaya, Zhur. Obshch. Khim., 32, 2161 (1961).
32. G. A. Razuvaev, Zhur. Vses. Khim. Obshch. im. Mendeleeva, 7, 325 (1962).
33. N. S. Vyazankin, G. A. Razuvaev, and T. N. Brevnova, Zhur. Obshch. Khim., 35, 2033 (1965).
34. G. A. Razuvaev, S. F. Zhil'tsov, and O. N. Druzhkov, Zhur. Obshch. Khim., 36, 258 (1966).
35. E. B. Milovskaya, E. I. Pokrovskii, and E. F. Fedorova, Izv. Akad. Nauk SSSR, Ser. Khim., 1093 (1967).
36. L. V. Zamoiskaya, E. B. Milovskaya, and V. A. Orestova, Izv. Akad. Nauk SSSR, Ser. Khim., 2053 (1970).
37. L. V. Zamoiskaya, Candidate's Thesis, Institute of Macromolecular Compounds, USSR Academy of Sciences, Leningrad, 1971.
38. G. A. Razuvaev and E. V. Mitrofanova, Zhur. Obshch. Khim., 38, 349 (1968).
39. G. A. Razuvaev, L. P. Stepovik, V. A. Dodonov, and G. V. Nesterov, Zhur. Obshch. Khim., 39, 123 (1969).
40. G. A. Razuvaev, V. N. Pankratova, V. A. Muraev, and I. B. Bykova, Zhur. Obshch. Khim., 39, 2490 (1969).
41. G. A. Razuvaev, V. A. Dodonov, and E. V. Mitrofanova, Zhur. Obshch. Khim., 39, 690 (1969).
42. E. L. Kopp, Candidate's Thesis, Institute of Macromolecular Compounds, USSR Academy of Sciences, Leningrad, 1970.
43. E. A. Kopp and E. V. Milovskaya, Izv. Akad. Nauk SSSR, Ser. Khim., 1949 (1971).
44. E. L. Kopp, O. S. Mikhailycheva, and E. B. Milovskaya, Vysokomol. Soed., A-14, 2653 (1972).
45. L. P. Stepovik, V. A. Dodonov, and L. A. Malygin, Zhur. Obshch. Khim., 39, 2043 (1969).
46. Kh. S. Bagdasar'yan, "Teoriya Radikal'noi Polimerizatsii" (Theory of Radical Polymerisation), Izd. Nauka, Moscow, 1966, p. 41.
47. F. A. Cotton and G. Wilkinson, "Advanced Inorganic Chemistry: A Comprehensive Text" (Translated into Russian), Izd. Mir., Moscow, 1969, Part I, p. 62.
48. N. A. Izmailov, "Elektrokhimiya Rastvorov" (Electrochemistry of Solutions), Izd. Kharkov. Gos. Univ., 1959, p. 308.
49. J. Contreras et al., J. Polymer. Sci., A-1, 7, 2341 (1969).
50. A. Davies, S. Hook, and R. Roberts, J. Organometall. Chem., 22, C-37 (1970).
51. N. Fetter and B. Bartocha, Canad. J. Chem., 40, 342 (1962).
52. A. Davies, B. Roberts, and J. Smith, Chem. Comm., 557 (1970).
53. J. Hollaender and W. Neumann, Angew. Chem., 83, 850 (1971).
54. A. Davies and S. Hook, J. Chem. Soc. (B), 735 (1970).
55. A. Davies and B. Roberts, J. Chem. Soc. (B), 1831 (1971).
56. J. Grotewold, E. Lissi, and J. Scaiano, J. Chem. Soc. (B), 1187 (1971).
57. T. Hirano, T. Miki, and T. Tsuruta, Makromol. Chem., 104, 230 (1967).
58. F. Arimoto, J. Polymer. Sci., A-1, 4, 275 (1966).
59. R. Kern and J. Schaefer, J. Polymer. Sci., B-5, 157 (1967).
60. P. Brindley and R. Pearson, J. Polymer. Sci., B-6, 831 (1968).
61. J. Grotewold, E. Lissi, and A. Villa, J. Polymer. Sci., A-1, 6, 3157 (1968).
62. E. Arancibia et al., J. Polymer. Sci., A-1, 7, 3430 (1969).
63. J. Furukawa and T. Tsuruta, J. Polymer. Sci., 28, 227 (1958).
64. T. Huff and E. Perry, J. Polymer. Sci., A-1, 1553 (1963).
65. L. V. Zamoiskaya, S. I. Vinogradova, and E. B. Milovskaya, Vysokomol. Soed., A-13, 1484 (1971).
66. P. Allen, B. Bateup, and B. Cassey, European Polymer. J., 8, 329 (1972).
67. H. Brown, M. Midland, and G. Kabalka, J. Amer. Chem. Soc., 93, 1024 (1971).
68. M. Midland and H. Brown, J. Amer. Chem. Soc., 93, 1506 (1971).
69. M. Midland and H. Brown, J. Amer. Chem. Soc., 93, 1508 (1971).
70. H. Brown, J. Amer. Chem. Soc., 90, 4166 (1968).
71. G. Kabalka et al., J. Amer. Chem. Soc., 92, 710 (1970).
72. G. Kabalka et al., J. Amer. Chem. Soc., 92, 714 (1970).
73. A. Suzuki et al., J. Amer. Chem. Soc., 93, 2792 (1971).
74. B. M. Mikhailov and Yu. N. Bubnov, Izv. Akad. Nauk SSSR, Ser. Khim., 2248 (1964).
75. H. Brown and M. Midland, J. Amer. Chem. Soc., 93, 3291 (1971).

Institute of Macromolecular Compounds,
USSR Academy of Sciences, Leningrad