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Electron Transfer as an Elementary Act of Organic Reactions

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Many heterolytic reactions are often accompanied by radical processes and contrariwise the reactions of radicals in many instances lead to the formation of ions. The simultaneous occurrence of homolytic and heterolytic processes cannot be explained from the viewpoint of the now generally accepted theory of organic reactions. These contradictions can be easily resolved if it is assumed that the formation of a new bond is preceded by the transfer of an electron from one reacting entity to another.

In the present work on the basis of voluminous literature material the conclusion is drawn that electron transfer processes actually play an important part in many organic reactions (reactions with free metals, some substitutions, etc.).

The influence of various factors on electron transfer processes is examined. Assumptions concerning the relative role of these processes in the formation and reactions of organometallic compounds are advanced. There is a bilbiography of 242 references.

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I. INTRODUCTION

Many of the concepts of contemporary theoretical chemistry built up in the first half of the XXth century and which are indisputably of use in chemistry need not now be regarded as absolute. This relates, for example, to attempts to positively divide reactions which really proceed according to a cyclic transfer scheme into electrophilic and nucleophilic[1,2]. Frequently on the basis of such a division one of the reacting species is essentially regarded arbitrarily as the "reagent" and the other as the "substrate". Dessy and Paulik[2] recently criticised the expediency of such a categoric classification for examples of a multicentre mechanism.

The same uncertainty arises also in attempts to divide strictly reactions into homolytic and heterolytic. Usually the problem of the homolytic or heterolytic nature of a process becomes unnecessary ultimately. In most instances only the fact of the formation of radical products in ionic reactions (or, contrariwise, the production of ions in free radical reactions) is stated but these processes are regarded as side-reactions which proceed in parallel with the main reaction.

Apparently such a contradiction can be resolved if it is assumed that the formation of a new bond is preceded by the transfer of electrons from one reacting species to another (by virtue of a difference in electron affinity and the greater mobility of the electron cloud in comparison with the nuclei or entire fragments of the molecules). Assumptions of this type are sometimes regarded as one of the possible approaches to the classification of organic reactions[3], but really these considerations have until recently not been taken into account in examining particular mechanisms.

In examining different electrochemical processes, Semenov[4] noted that "... strictly speaking, in a single act one electron is transferred, since the simultaneous transfer of two electrons is a much less probable event". Despite the considerable differences between chemical changes and electrode processes, this position, it seems to us, must be taken into account in studying organic reactions when the sources of electrons are metals, ions, or neutral molecules.

Heterolytic breaking of a non-ionic bonds with not too pronounced solvation effects is energetically less favourable than homolytic breaking, since in the first instance additional energy is needed for the preliminary polarisation of the bond[5,6]. More and more information is becoming available showing that the so-called homolytic dissociation is usually a minimum bimolecular process[7,8] and one of the reagents can also serve to localise an electron[9].

Electron transfer is a widely distributed phenomenon in inorganic redox reactions and various photochemical and radiation-chemical processes[10,11].

Finally, extensive although insufficiently systematised material about organic reactions of electron transfer is being accumulated and the tempo of the increase in new facts in this region is so high that the idea naturally arises that reactions of this type actually permeate the whole of organic chemistry including the field of "classical" heterolytic reactions.

This article is an attempt to generalise and systematise these facts, although it is hardly possible to deal with them exhaustively within the framework of the present review.

II. FORMATION OF STABLE RADICAL-IONS

The most typical electron transfer reactions, where the very fact of the transfer of just one electron is unquestioned, are reactions for the formation of radical-ions (RI). Since in this instance the electron transfer is usually not complicated by side-processes and the RI itself is readily identified by EPR methods and ultraviolet spectroscopy, these reactions are an extremely convenient model for studying electron transfer in organic reactions. Some typical examples of monoelectron transfer reactions are given in Table 1.

Table 1. Types of electron transfer.

Reaction	Electron donors	Electron acceptors (EA)
Reduction by metals	M = alkali or alkaline earth metals or its amalgam	aromatic and heterocyclic compounds, arylalkyl and diaryl ketones, imines of diaryl ketones, nitro-compounds, some organoelemental compounds
Electrochemical reduction	cathode	ditto
Electrochemical oxidation	aromatic hydrocarbons, amines	anode
Reduction by anions	organometallic compounds of active metals, alkoxides, iodide ion	aromatic compounds, diaryl ketones, aromatic diazo-compounds, tetracyanoethylene, nitro-compounds
Reduction by Lewis bases	aromatic hydrocarbons, amines, alkenes	nitro-compounds, tetracyanoethylene, stable radicals, carbonium ions
Oxidation	aromatic hydrocarbons, amines, metallocenes, free radicals	conc. H_2SO_4, $AlCl_3 + CH_3NO_2$, $SbCl_5$, tetracyanoethylene, heavy metal cations, nitro-compounds

A large number of organic compounds of different classes exhibit the capability to receive one electron with the formation of anionic radicals (AR).[12] This relates to aromatic[13-16] and heterocyclic[11-20] systems and also to systems which contain conjugated bonds[21-23] and electron-withdrawing groups[24,25]. Initial reports of the production of AR of cyclopropane, adamantane, hexamethylenetetramine, spiropentane, and 1-methyladamantane proved erroneous[26].

Reports recently appeared about the production of a series of organoelemental AR, containing boron[27,28], silicon[29,30], germanium[30], nitrogen[31,32], phosphorus[33-35], and transition metals[36].

Under the action of oxidants, aromatic[37] and heterocyclic[38] compounds and also some amines[39-40] can give up one electron to form cationic radicals (CR).

1. Reduction by Metals

Historically the first and therefore now the most developed method of production of stable AR are reactions with free metals. The ease of formation of AR depends on a series of factors, the most important of which are the affinity of the acceptor for an electron, the solvating capability of the medium, and the donor ability of the electron source. In a series of aromatic hydrocarbons the capability for reduction rises on going from benzene to condensed aromatic hydrocarbons: benzene < biphenyl < < naphthalene < anthracene < tetracene[41,42]. The introduction of electron-withdrawing substituents also acts in the same direction. The ease of transfer of an electron to the molecule of the acceptor from a metal is determined by the donor capability of the latter. However, the quantitative evaluation of this capability encounters considerable difficulties: in particular it is impossible to use standard electrode potentials in water, the photochemical work function, etc. In most instances alkali or alkaline earth metals or their amalgams[12] are used for reduction, but when the acceptor molecule has a sufficiently high electron affinity heavy metals can also act as reductant. For example, tetracyanoethylene forms an AR on reduction with copper powder[43]:

$$(CN)_2C{=}C(CN)_2 + Cu \rightarrow [(CN)_2C{=}C(CN)_2^{\cdot-}Cu^+ .$$

In the alkali metal series lithium seems the best reductant for most instances. In dimethoxyethane the reaction of biphenyl with sodium is equilibrium ($K \simeq 10^{-2}$),[44] whereas a dianion is formed with lithium under these conditions[45]:

$$C_{12}H_{10} + Na \underset{}{\overset{DME}{\rightleftharpoons}} C_{12}H_{10}^{\cdot-} + Na^+$$

$$C_{12}H_{10} + Li \xrightarrow{DME} C_{12}H_{10}^{2-} + 2\,Li^+ .$$

This can be explained by the greater solvation of the lithium cation compared with the cations of its analogues in the Group[46], which appears, in particular, in the fact that lithium, unlike sodium, is soluble in tetrahydrofuran[47]. In the general case the ease of formation of similar AR in various ethers changes symbathically with the solubility in these ethers of alkali metals or of K/Na alloy[47-53]. Probably, in the formation of the AR the solvent plays the part of a carrier of an electron from the metal to the molecule of the acceptor†. Hexamethyltriamidophosphate exhibits the greatest dissolving ability in relation to alkali metals (up to 1 M),[53,54] however, unfortunately the influence of this solvent on the formation of AR has not yet been studied. The important and sometimes also the decisive part of the medium in the formation of AR can be illustrated by a series of examples. Thus whereas in DME naphthalene is reduced by sodium to an AR,[57] in liquid ammonia a dianion is formed[58]. Similarly magnesium does not reduce naphthalene in ethers, whereas in liquid ammonia naphthalenemagnesium is formed[59]; trimesitylboronsodium, which exists in benzene solution as a diamagnetic dimer, dissociates on the addition of tetrahydrofuran[27].

2. Electrochemical Reactions

A review was recently published about the mechanism of electrochemical reactions[60], therefore we will consider here only certain examples dealing with the formation of RI in electrode processes. AR of naphthalene[61], anthracene, biphenyl, chrysene, fluoranthene[62], azulene[63], substituted benzenes[63], benzophenone[64], and fluorenone[65] were obtained by electrochemical reduction.

In many instances electrochemical methods have definite advantages over other methods of generating AR.[40,66]

† It is known, however, that potassium also reacts with aromatic compounds in a hydrocarbon medium[55,56].

Carrying out the electrolysis in the microwave cavity of an EPR spectrometer allowed extremely unstable IR to be identified, the experimental detection of which by other methods would be extremely complicated. This relates, for example, to the production of the AR of butadiene[21] and certain organoelemental compounds[36], and the CR of *p*-phenylenediamine[66] and triethylenediamine[40]. The use of electrochemical methods allowed the effect of various solvents (including protic solvents) on the distribution of unpaired electron density in various AR to be investigated[68,69]. In several instances EPR spectra with a high degree of resolution were obtained[70].

Interesting results have been obtained in investigating the polarographic reduction of halogenonitrobenzenes[71]. It was found that with iodonitrobenzenes only the spectrum of the AR of nitrobenzene is observed, whereas the formation of an AR precedes the loss of an iodide ion. With the bromonitrobenzenes a bromide anion is detached only from the *ortho*-position; chloronitrobenzenes form stable AR. In drawing attention to the undoubted similarity between electrochemical reduction and reactions with free metals it can be suggested that the first act in the reduction of halogen derivatives by metals is also the transfer of an electron and the formation of AR (see p. 962).

3. Anions as Donors of an Electron

A large number of examples are known when the donors of an unpaired electron are diamagnetic anions: carbanions[72-77], dihydro-derivatives of aromatic compounds in the presence of bases[78,79], alkoxide ions[80,81], the hydroxide ion[82,83], and the iodide ion[84].

An acceptor of an unpaired electron can be neutral molecules (A)

$$B^- + A \rightarrow B^{\cdot} + A^{\cdot -}$$
$$B^{2-} + A \rightarrow B^{\cdot -} + A^{\cdot -};$$

free radicals formed with sufficient electron affinity:

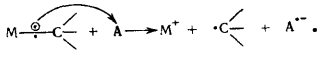
$$B^- + R^{\cdot} \rightarrow B^{\cdot} + R^-$$
$$B^{2-} + R^{\cdot} \rightarrow B^{\cdot -} + R^-;$$

ions:

$$B^- + R^+ \rightarrow B^{\cdot} + R^{\cdot}$$
$$B^- + B^{1-} \rightarrow B^{\cdot} + B$$

etc.

The potential carbanion of active organometallic compounds can also play the part of anions B^-, that is, in other words, a polar metal–carbon bond:

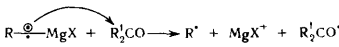


Apparently the first established instance of the transfer of a single electron from an anion to a neutral organic molecule is a reaction studied by Schlenk and coworkers[85,86], that between triphenylmethylsodium and diaryl ketones, leading (after hydrolysis and oxidation by atmospheric oxygen) to triphenylmethyl peroxide and pinacones:

$$(C_6H_5)_3C^- + Ar_2CO \rightarrow (C_6H_5)_3C^{\cdot} + Ar_2\dot{C}-\bar{O}.$$

Triphenylmethylmagnesium bromide reacts similarly[87].

The suggestion made by Arbuzov and Arbuzova about the free radical nature of the reaction of cyclohexylmagnesium bromide with benzophenone[88] is essentially equivalent to an assumption concerning the possibility of single-electron transfer in the reaction of Grignard reagents with ketones:



Indirect arguments in support of the stepwise nature of such reactions were found in subsequent years. The intermediate formation of ketyl was recently proved by the EPR method by the example of the reaction of a series of substituted benzophenones with ethylmagnesium iodide and phenylmagnesium bromide[76].

A single-electron transfer was observed in the reaction of triphenyltinlithium with benzophenone, carbon dioxide, and sulphur dioxide[74]. Streitwieser and Lawler noted the formation of AR of anthracene in investigating deuterio-exchange, which can be catalysed by lithium cyclohexylamide[89].

Organolithium compounds reduce certain aromatic hydrocarbons (for example, anthracene[77]) with the formation of the corresponding AR:

$$RLi + ArH \rightarrow R^{\cdot} + Li^+ + ArH^{\cdot -}.$$

The ability of organolithium compounds to transfer a single electron changes symbatically with their ease of oxidation[90], evidently by virtue of the similarity in the mechanisms of these reactions. For example, in going from primary to secondary, and further to tertiary radicals R, the rate of oxidation and the ease of electron transfer increase. According to Russell, this is connected with the decrease in the stability of the carbanion and the increase in the stability of the corresponding radical in this series. It is characteristic that the AR of tolane could be observed in the action of t-butyl-lithium on tolane but not of n- or s-butyl-lithium[91].

Table 2. Decomposition potentials of Grignard reagents in 1 M ethereal solution.

R in RMgX	Decomposition potential, V	R in RMgX	Decomposition potential, V
C_6H_5	2.17	$C_6H_5(CH_3)CH$	1.24
CH_3	1.84	$(CH_3)_2CH$	1.07
C_3H_7	1.42	$(CH_3)_3C$	0.97
C_4H_9	1.32	$CH_2{=}CHCH_2$	0.86
C_3H_5	1.28		

A searching quantitative appraisal of the donor ability of organometallic compounds can evidently be obtained by using their electrochemical oxidation potential, but information on this question is scanty[92-94]. Evans[92,93] determined the decomposition potentials of ethereal solutions of alkylmagnesium halides (Table 2). If it is assumed that in a series of corresponding organo lithium compounds an analogous picture will be obtained, then it can be expected that depending on the type of radical the donating ability of the alkyl-lithiums will increase in the order: CH_3 < higher alkyls < allyl < benzyl. Actually, the rate of formation of the AR increases in the order CH_3Li, $C_6H_5Li \ll C_4H_9Li < C_6H_5CH_2Li$.[73]

The transfer of an unpaired electron from an organometallic compound is greatly increased under ultraviolet irradiation, Thus on irradiating the C_6H_5Li–ArH system the rate of formation of the AR $ArH^{\cdot -}$ is increased by a factor of 10^5.[75]

An important condition for the single-electron transfer from an anion to a neutral molecule is a sufficiently great difference between the values of the electron affinity of the donor and the acceptor. As noted above, organolithium

compounds reduce aromatic hydrocarbons[77], and organomagnesium compounds reduce diaryl ketones[76,95]. Although apparently weaker reductants than organometallic compounds of the active metals, nevertheless alkoxide ions are capable of reducing aromatic ketones and nitro-compounds[80,95].

The reduction of diaryl ketones and nitro-compounds by alkoxides is also accelerated by irradiation, and the concentration of the AR formed is determined by the intensity of the irradiation[96]:

$$ArNO_2 + RO^- \xrightarrow{h\nu} ArNO_2^{\cdot -} + RO^\cdot$$

$$Ar_2CO + RO^- \xrightarrow{h\nu} Ar_2CO^{\cdot -} + RO^\cdot.$$

Tetracyanoethylene[43] and tetracyanoquinodimethane[98], which exhibit a very high electron affinity, are readily oxidised by even the iodide ion:

$$I^- + (CN)_2C{=}C(CN)_2 \rightarrow {}^1/_2 I_2 + [(CN)_2C{=}C(CN)_2]^{\cdot -}$$

$$I^- + (CN)_2C{=}\langle\rangle{=}C(CN)_2 \rightarrow {}^1/_2 I_2 + \left[(CN)_2C{=}\langle\rangle{=}C(CN)_2\right]^{\cdot -}.$$

The hydroxide ion reacts similarly, also reducing *p*-quinone, chloroanil, and duroquinone[82,83,97,99].

Many acetylenic compounds are also rather strong acceptors in relation to the anions I^-, CN^-, and SCN^- in dimethylformamide medium[100]:

$$A^- + RC{\equiv}CR' \rightarrow [RC{\equiv}CR']^{\cdot -} + A^\cdot$$

where A = I, CN, or SCN.

It was noted above that in the dissolution of aromatic nitro-compounds in alcohol–dimethylsulphoxide mixture in the presence of alkali metal alkoxide the EPR signal of the corresponding AR is observed, but the degree of electron transfer‡ is relatively low (~ 0.1%). Since under these conditions many conjugated acids are converted into anions this allowed us to evaluate the relative donating ability of a series of anions[95] (Table 3). The data in Table 3, however, allow only an approximate estimation of the relative donor ability of the various sources of an unpaired electron, since these values are greatly dependent upon the degree of ionisation of the initial compound under the action of an alkoxide:

$$BH + RO^- \rightarrow B^- + ROH,$$

and also of the side-reactions, the importance of which depends upon the nature of the donor. The nature of the acceptor is also far from being unimportant. Thus in relation to nitrobenzene, cyclopentadienes are arranged in the order: cyclopentadiene < fluorene < indene, whereas in relation to azobenzene the order is different: cyclopentadiene < indene < fluorene[95]. Whereas organolithium compounds are frequently better reductants than the corresponding organomagnesium compounds the observable degree of electron transfer in benzofurazane and benzo[*c*]indolene is significantly greater for alkylmagnesium halides.

The restrictions associated with side-processes which accompany the transfer of an electron from an anion to an acceptor molecule are reduced to a minimum in studying electron transfer reactions between dianions and the corresponding hydrocarbons[42,101,102]:

$$B^{2-} + B \rightarrow 2B^{\cdot -}.$$

In many instances instead of dianions it is possible to use the corresponding dihydro-derivatives in the presence of strong bases[78,103–108]. Exceptions are the 1,4-dihydronaphthalene–naphthalene and 1,4-cyclohexadiene–benzene systems in which the AR were not observed. This departure is evidently explained by the fact that under these reaction conditions ionisation of the 1,4-dihydronaphthalene and 1,4-cyclopentadiene does not take place.

‡ The degree of electron transfer = [AR] × 100/[acceptor] %.

Table 3. Degree of electron transfer* from anions to aromatic nitro-compounds.

Donors[a]	Acceptor[b], degree of electron transfer, % (5 min)	
	nitrobenzene[c]	m-dinitrobenzene[d]
Pure solvent	0.1 (10 min)	0.1 (20 min)
Fluorene	13	40.80 (2 min)
Indene	36	—
Cyclopentadiene	0.8	2.6
Acetophenone	0.8	2.7
Propiophenone	91	4
Benzoin	100[f]	—
Bluoren-9-ol	100[f]	—
1,4-Hydroquinone	40[f]	100[f]
Thiophenol	0.2 (30 min)	0.6
3,4-Dimercaptotoluene	11	58
Nitroethane	0.6	2
N-Hydroxybenzenesulphamide	92	10[e] (10 min)
Hydrazobenzene	2 (40 min)	7.5[e] (2 min)
Benzophenone ketyl[h]	100	6.8 (3 min)
n-Butyl-lithium[i]	6	

* See note

a) Concentration of donor 0.025 M, concentration of base 0.05 M;
b) Concentration of acceptor 0.005 M.
c) Dimethyl sulphoxide (20%)–t-butyl alcohol (80%).
d) In ethanol (EPR spectrum does not correspond with the AR of the acceptor
e) [Not given in Russian (Ed. of Translation)].
f) EPR spectrum of the AR of the donor predominates.
g) Spectra of both AR are observed.
h) Obtained in the dissociation of saturated solution of benzpinacone.
i) 1 M solution in a mixture of tetrahydrofuran (75%) and hexane (25%).

Stable radicals are effective electron acceptors but reactions of this type have hardly been studied at all. From the broadening of the hyperfine structure lines of the EPR spectrum Weissmans and coworkers[109] found the presence of electron exchange between the tris-(*p*-nitrophenyl)methyl radical and the corresponding anion:

$$(p\text{-}NO_2C_6H_4)_3C^\cdot + (p\text{-}NO_2C_6H_4)_3C^- \rightleftarrows (p\text{-}NO_2C_6H_4)_3C^- + (p\text{-}NO_2C_6H_4)_3C^\cdot.$$

Depending on the solvent the rate constant varies within the limits 10^7–10^9 litre mole^{-1} s^{-1} and the activation energy from 0.9 to 2.3 kcal mole^{-1}.

4. Neutral Molecules as Donors of an Electron

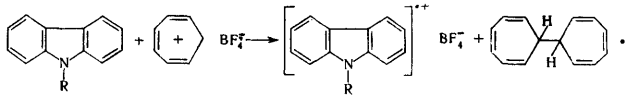
A large number of aromatic and heterocyclic compounds, and also compounds which contain a hetero-atom, have an unshared pair of electrons (many, a nitrogen atom) capable of acting as a donor of an electron in relation to a strong oxidant, forming a CR.

For example, triphenylamine is readily oxidised by iodine in the presence of silver perchlorate with the formation of a coloured paramagnetic solution of triphenyliminium perchlorate $(C_6H_5)_3NH^{\cdot +}ClO_4^-$.[110] Other aromatic amines behave similarly[111,112]. CR of *p*-phenylenediamine[66,67] and its alkyl-substituted derivatives[39,113], triethylenediamine[40], tetrakis(dimethylamino)ethylene[114], and several other amines were obtained by electrochemical oxidation.

Electron transfer was observed for the reaction between aliphatic amines and trinitrobenzene[113,115], tetracyanoethylene, and tetracyanoquinodimethane[116]. Many complexes of aromatic amines are paramagnetic even in the solid state. The complexes of tetramethyl-*p*-phenylenediamine with benzoquinones and tetracyanoquinodimethane dissociate in solvating solvents, forming the corresponding CR and AR.[78,117,118] The complexes of tetracyanoethylene[43,66] behave similarly. Tetramethyltetrazene is oxidised by tetranitromethane into the corresponding CR:[119]

$$(CH_3)_2NN{=}NN(CH_3)_2 + C(NO_2)_4 \rightarrow [(CH_3)_2NN{=}NN(CH_3)_2]^{\cdot +} + [C(NO_2)_4]^{\cdot -}.$$

Carbonium ions can act as the electron acceptor. Thus tropylium tetrafluoroborate oxidises carbazole and *N*-methylcarbazole to the corresponding CR:[120]

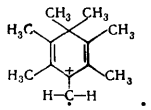


The CR themselves can act as oxidants in relation to other amines having less electron affinity than amines corresponding to the given CR. Thus the CR of *NN'*-tetramethylbenzidine is reduced by *p*-phenylenediamine and its *NN'*-tetramethyl derivative[121]:

$$[(CH_3)_2NC_6H_4C_6H_4N(CH_3)_2]^{\cdot +} + (CH_3)_2NC_6H_4N(CH_3)_2 \rightarrow (CH_3)_2NC_6H_4C_6H_4N(CH_3)_2 + [(CH_3)_2NC_6H_4N(CH_3)_2]^{\cdot +}.$$

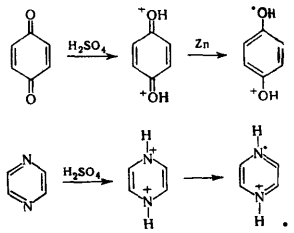
The oxidation of aromatic and heterocyclic compounds can be brought about both electrochemically and by chemical means[122-125].

The oxidants used are: 98% sulphuric acid[126,127], alkyl- or aryl-sulphonic acids[128], antimony(V) chloride[129,130], and aluminium chloride in nitromethane solution[131]. Sulphuric acid is a relatively weak oxidant, therefore the CR concentration is usually low. Thus with anthracene only 1% of the total amount of hydrocarbon introduced is oxidised. With $SbCl_5$ the oxidation is almost complete. In the action of $SbCl_5$ on an excess of anthracene in methylene chloride an adduct of CR with the neutral molecule is formed $(C_{10}H_{12})_2^{\cdot +}SbCl_4^-$.[130] When sulphuric acid acts on hexamethylbenzene a CR related to the heptamethylbenzonium cation is formed[132]:



The same CR is formed in the reaction of iodine and antimony(V) chloride.

The CR of the semiquinone type are formed in the reduction of dicarbonyl compounds and of related nitrogen heterocycles in an acid medium[133]. For example, for *p*-benzoquinone and piperazine:



Analogous CR are obtained from 1,4-naphthoquinone, anthraquinone, phenazine, 4,4'-bipyridyl, and certain α-diketones[134-136].

Strong π-acids of the tetracyanoethylene (TCNE) and tetracyanoquinodimethane (TCQ) type react with aromatic hydrocarbons to form the corresponding AR and CR:[43,98]

$$ArH + TCNE \rightarrow ArH^{\cdot +} + TCNE^{\cdot -}$$

With tetracyanoquinodimethane, complexes of the composition $ArH^+(TCNQ)^-$ (TCNQ) are also formed[98].

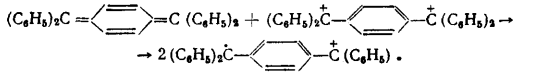
The biscyclopentadienyls of cobalt and iron are oxidised by TCNE and 2,3-dichloro-5,6-dicyano-*p*-benzoquinone to the corresponding metallocinium cations[107,137]:

$$(C_5H_5)_2M + TCNE \rightarrow (C_5H_5)_2M^+ + TCNE^{\cdot -}$$

where M = Fe, Co. The position of the equilibrium depends greatly on the solvent[137].

The formation of paramagnetic products, probably the result of electron transfer, was noted in the reaction of tetranitromethane with 2,3-dimethylbutadiene, cyclohexadiene, and isoprene[138].

One of the reliably established examples of the donor capability of a conjugated system of double bonds is the single-electron transfer from tetraphenylquinodimethane to a dicarbonium ion from tetraphenyl-*p*-xylene[139]:

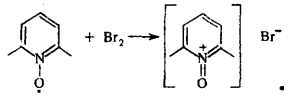


5. Radicals as Donors of an Electron

Free radicals, which exhibit high electron affinity usually emerge as vigorous oxidants. However, the available experimental data suggest that free radicals in the accepted sense are amphoteric, that is, capable both of capture of an electron not supplied to the carbanion and of the supply of an unpaired electron to a sufficiently strong acceptor with the formation of a corresponding cation. The best known example of the donor ability of free radicals is the reduction of heavy metal salts by the triphenylmethyl radical[140]:

$$Ph_3C^{\cdot} + AgClO_4 \rightarrow Ph_3C^+ClO_4^- + Ag.$$

Stable *N*-oxide radicals are readily oxidised by bromine to form immonium cations[141]:



Bulê and Norman[142], in investigating the reaction of formaldehyde and acetaldehyde with hydroxyl radicals, found that with an excess of the aldehyde the EPR spectrum of the AR of the corresponding aldehyde is observed. On adding nitrobenzene to the reaction mixture the EPR spectrum of a nitrobenzene AR was observed. These results formed a basis for the hypothesis that a hydrated form of a primary radical, produced in the removal of a hydrogen atom from a molecule of the aldehyde, is capable of reducing a neutral molecule of the aldehyde or nitrobenzene:

$$RCH(OH)_2 + \cdot OH \rightarrow RC(OH)_2,$$
$$R\dot{C}(OH)_2 + RCHO \rightarrow RCO_2H_2^+ + R\dot{C}HO \rightleftarrows RCOOH + R\dot{C}HOH,$$

or

$$R\dot{C}(OH)_2 + C_6H_5NO_2 \rightarrow RCO_2H_2^+ + C_6H_5NO_2^{\cdot -}.$$

III. REACTIONS OF RADICAL-IONS

The reactions of RI, the high chemical activity of which is due to the presence of an unpaired electron, can be divided into two groups. The first type comprises the reactions in which RI participate only as donors (or acceptors) of an electron (reactions with organic halides, the initiation of polymerisation, exchange reactions, etc.). During the course of these reactions the skeleton of the RI molecule does not undergo any changes. The second class of reaction includes a large number of conversions of RI which lead to a fundamental reconstruction of the initial molecule (hydrolysis, alkylation, decomposition of the RI, etc.).

1. Radical-ions as Donors and Acceptors of an Electron

Typical representatives of this type of reaction are the exchange reactions of RI with neutral molecules[121,143-145]:

$$ArH + ArH^{\cdot-} \rightleftarrows ArH^{\cdot-} + ArH,$$
$$ArH^{\cdot+} + ArH \rightleftarrows ArH + ArH^{\cdot+}.$$

Weissmann and coworkers[143] first showed that exchange by an electron appears in a broadening of the hyperfine structure lines of the EPR signal, the increase in breadth depending significantly on the concentration of the neutral compound. The changes in the EPR spectra were used to calculate the rate constants of the exchange[144,145]. Exchange reactions between stable AR and various acceptors[40,41,122] of the type:

$$ArH^{\cdot-} + Ar'H \rightleftarrows ArH + Ar'H^{\cdot-}$$

were also studied and it was shown that the position of the equilibrium depends on the difference in potentials of the polarographic reduction of the two partners[121].

Reactions of AR with organic halides have been studied in the greatest detail. In these reactions the AR act as an effective donor of an electron. The primary act of the reaction is the transfer of an electron from the AR to the halide molecule with the formation (probably through the intermediate formation of an AR of the halogen derivative) of a hydrocarbon radical and a halide ion[146-149]:

$$ArH^{\cdot-}M^+ + RX \rightarrow ArH + [RX^{\cdot-}M^+] \rightarrow R^{\cdot} + X^- + M^+.$$

The subsequent fate of radical R is determined by its structure and the conditions under which the process is carried out. In carrying out the reaction of the AR of naphthalene with an equimolecular mixture of two alkyl halides, RX and R'X, a mixture of the hydrocarbons RR, RR', and R'R' is formed in the ratio 1 : 2 : 1, together with appreciable quantities of RH and R_{-H}.[147] The ratio of the products of dimerisation (R–R) and of the products of the reaction of the radical with the solvent depends greatly on the nature of the halogen atom. Thus in the system $n\text{-}C_5H_4X + C_{10}H_8^{\cdot-}Na^+$, on going from n-pentyl chloride to the iodide the quantity of n-pentane decreases from 43.9 to 17.3% and the yield of n-decane increases from zero to 55.7%. The reaction of hexenyl halides with naphthalene-sodium is accompanied by a rearrangement of the hexenyl radical formed into the cyclopentylmethyl radical[149]. With certain aromatic and aliphatic-aromatic halides the reaction with the AR leads to products of a Wurtz reaction with rather high yields (bibenzyl 30, bibenzhydryl 71, bi-2-naphthyl 71, biphenyl 90%)[148]; the initial aromatic hydrocarbon can be used in catalytic amounts.

Spectrophotometric investigation of the reactions of AR with various alkyl halides showed that the reaction is second order overall, first with respect to each of the reagents[150-152].

Since during the course of the reaction the organically bound halogen is converted into a halide ion, this method could be used for the quantitative determination of halogen in organic compounds[153,154].

Alkyl tosylates are split by the naphthalene AR with formation of the corresponding alkoxides and salts of toluene sulphinic acid. The yield of alcohols (after hydrolysis) is almost quantitative. Under the action of an excess of AR the sulphinic acid is reduced to toluene[155]:

$$p\text{-}CH_3C_6H_4SO_3OR + C_{10}H_8^{\cdot-}Na^+ \rightarrow p\text{-}CH_3C_6H_4SO_2^-Na^+ + RONa \xrightarrow{\text{excess } C_{10}H_8^{\cdot-}Na^+} CH_3C_6H_5.$$

Under the action of inorganic oxidants the AR also very readily give a surplus electron. In oxidation by atmospheric oxygen the original hydrocarbon and the alkali metal peroxide are formed, for example[156]

$$2C_{10}H_8^{\cdot-}Na^+ + O_2 \rightarrow 2C_{10}H_8 + Na_2O_2.$$

Under these conditions cobalt(II) chloride is reduced with the formation of colloidal cobalt, which ignites in air[157]. The reducing action of AR finds application for obtaining highly reactive manganese, used for making manganese carbonyl[158].

2. Reaction of Radical-ions Accompanied by a Change in the Structure of the Initial Molecule

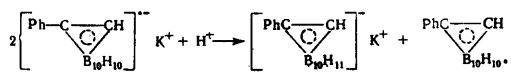
The overwhelming majority of AR are stable only in aprotic media. The addition of protic solvents causes a rapid disappearance of a characteristic signal in the EPR spectrum. With the AR of aromatic hydrocarbons the main products are the corresponding dihydro-derivative and the initial hydrocarbon (mixture ~ 1 : 1):[156,159]

$$ArH^{\cdot-} + H^+ \rightarrow ArH_2^{\cdot},$$
$$ArH_2^{\cdot} + ArH^{\cdot-} \rightarrow ArH_2^- + ArH,$$
$$ArH_2^- + H^+ \rightarrow ArH_3.$$

In the addition of a proton to the AR of an aromatic hydrocarbon the $ArH_2^{\cdot}$ radical is formed, which exhibits a greater electron affinity than the molecule of the initial hydrocarbon[160], which is subsequently reduced further by the excess of AR to the corresponding anion. If the anion formed is sufficiently stable (as it is, for example, in the alcoholysis of triphenylboronsodium) the reaction stops at this stage[161]:

$$2Ph_3B^{\cdot-}Na^+ + CH_3OH \rightarrow [Ph_3BH]\,Na + [Ph_3BOCH_3]\,Na.$$

The hydrolysis of the AR of phenylbarene proceeds analogously[162]:



The hydrolysis of ketyls can proceed in two directions, depending on the pH of the medium: in an acid medium the corresponding pinacones are formed[163], whereas hydrolysis in a neutral medium leads to a mixture of a ketone and an alcohol[164]:

$$Ar_2C(OH)-C(OH)Ar_2 \xleftarrow{H^+} 2Ar_2\dot{C}-O^- \xrightarrow{H_2O} Ar_2C{=}O + Ar_2CHOH.$$

The hydrolysis of dianions of aromatic hydrocarbons which are formed during the subsequent reduction of the

AR leads to the same products as the hydrolysis of the AR:[165,166]

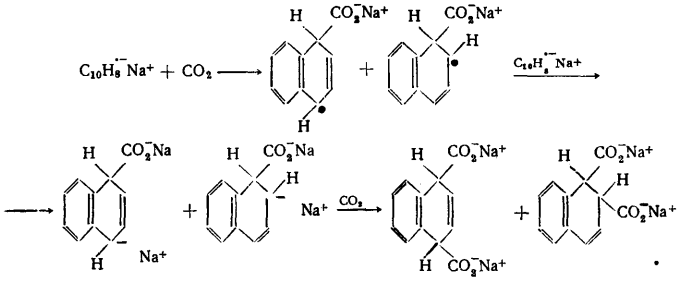
$$ArH^{2-} + H^+ \rightarrow ArH_2^-,$$
$$ArH_2^- + H^+ \rightarrow ArH_3.$$

The mono-anions which are formed in the addition of a proton to a dianion are identical with anions formed in the hydrolysis of the AR. Depending on the nature of the initial hydrocarbon these monoanions disproportionate in solution by one of the following schemes:

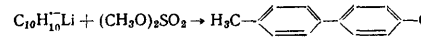
$$2ArH_2^- \rightarrow ArH_3 + ArH^{2-},$$
$$2ArH_2^- \rightarrow ArH_3^- + ArH^-.$$

The stable AR can also detach a proton from extremely weak acids, entering into the role of effective metallating agents[67,167,173]. Thus Normant and Angelo[67] used naphthalenesodium for the metallation of carboxylic acids and their salts. The yields of the corresponding malonic acids (after carboxylation) reached 80%.

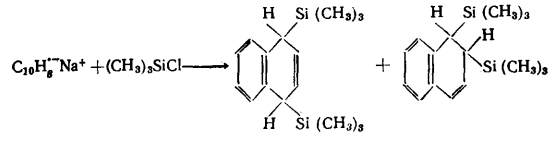
The carboxylation of AR, like hydrolysis, leads to the formation of dihydro-derivatives of the initial aromatic hydrocarbons[168,169]. For example, a mixture of 1,2- and 1,4-dihydronaphthalenedicarboxylic acids is obtained from the AR of naphthalene:



Unlike the reactions of aromatic AR with alkyl halides considered in the previous section, the reaction of dimethyl sulphate with the AR of biphenyl leads to the formation of a dimethylated product[170]:

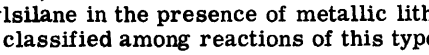


Chlorotrimethylsilane reacts similarly with the AR of naphthalene[171]:



1,2- and 1,4-isomers are formed in the approximate ratio of 1 : 2.

Evidently, the formation of bis-3,6-(trimethylsilyl)-cyclohexa-1,4-diene in the reaction of benzene with chlorotrimethylsilane in the presence of metallic lithium[172] must be classified among reactions of this type:



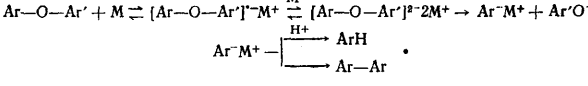
The reactions with toluene and anisole proceed similarly.

IV. REACTIONS WHICH PROCEED THROUGH THE INTERMEDIATE FORMATION OF RADICAL-IONS

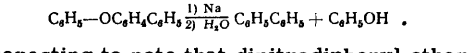
The development of physicochemical methods of investigation, and above all of EPR, gave the possibility of tracing the formation, and in some instances also the kinetics, of the accumulation and decomposition of short-lived AR during chemical reactions. The results obtained are undoubtedly of considerable interest in themselves but in addition they clearly show the large part which electron transfer processes play in various chemical changes.

1. Cleavage of Carbon–Element Bonds

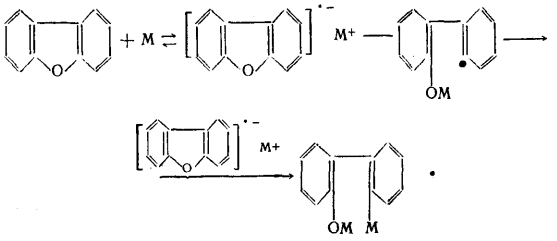
The cleavage of diaryl and alkyl aryl ethers by alkali metals has long been known[174] and in some instances finds synthetic application for the production of compounds containing a free hydroxyl group, but the mechanism of this process has still not been established. Recently, Eargle[175] and Strojny[176] showed that the first act of the reaction is the transfer of an electron from the alkali metal atom to the ether molecule with the formation of an AR; the latter takes a second electron, forming a dianion, the decomposition of which also leads to the products of the reaction:



The direction of the splitting of the dianion into different Ar and Ar′ depends on the nature of the aromatic radical[176]. For example, with biphenylyl phenyl ether, phenol and biphenyl are formed:

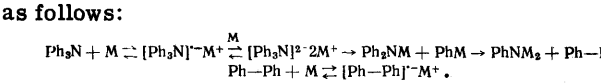


It is interesting to note that dinitrodiphenyl ether does not cleave under the conditions of the experiment[175]. This is evidently due to the delocalisation of an unpaired electron on the nitrogen atoms of the nitro-groups, which leads to the decrease in the electron density on the oxygen atom. The splitting of the C–O bond in dibenzofuran takes place at the AR stage. The radical formed as a result of the breaking of the bond is rapidly reduced by another molecule of AR into the corresponding anion[177]:



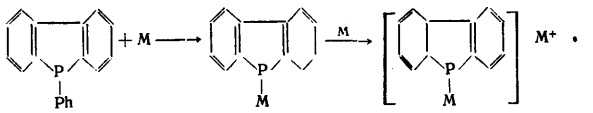
The kinetics of the decomposition of the AR was measured from the change in the intensity of the EPR signal. The activation energy depends slightly on the nature of the metal (19.0 kcal mole^{-1}). Splitting with alkali metals and other heterocyclic compounds evidently proceeds in a similar manner.

In investigating the splitting of compounds of the type Ar_3E (where E = N or P) by alkali metals the formation of a primary AR of the type $[Ar_3E]^-M^+$ has not yet been established (see Eliseeva and coworkers[35]). Thus with triphenylamine the only identifiable paramagnetic product is the AR of biphenyl[178]. The probable scheme of the decomposition, as for the diaryl ethers, can be represented as follows:



The splitting of triphenylphosphine[33] stops at the first stage with the formation of Ph_2PM, which is reduced by an excess of the metal to the dianion radical $[Ph_2PM]^{\cdot -}M^+$.

Biphenylylene(phenyl)phosphine [9-phenyl-9-phosphafluorene] reacts similarly with alkali metals[34]:



The metallation of aromatic hydrocarbons containing "acid" hydrogen atoms also proceeds through the stage of formation of AR.[179-181] It has been shown, by the example of indene and fluorene, that the AR formed can either decompose with the loss of a hydrogen atom, or detach a proton from a neutral molecule:

$$ArH + M \rightleftarrows ArH^{\cdot-}M^{+}$$

$$ArH^{\cdot-}M^{+} \rightarrow ArM + H^{\cdot}$$

$$ArH^{\cdot-}M^{+} + ArH \rightarrow ArM + ArH_{-H}^{\cdot}.$$

Which direction predominates depends on the nature of the initial hydrocarbon and the alkali metal. A unimolecular decomposition is catalysed by iron(II) salts[180].

Evidently, just the same happens in the breaking of the N–H bond. Thus, in the action of metallic potassium on carbazole in a medium of dimethoxyethane at low temperature the formation of an AR was established[182]; it was converted on heating into carbazylpotassium with the liberation of hydrogen. Solutions of the alkali metals in amines also slowly liberate hydrogen, forming the corresponding amides. It is interesting to note, that as for the AR of fluorene, this decomposition is accelerated by iron(II) ions.

Summarising all that has been said above, the general conclusion can be drawn that reactions with free metals start with the transfer of an unpaired electron to a molecule of another reagent with the formation of an AR, the subsequent conversion of which also determines the occurrence of the process as a whole.

This general position can, we consider, be extended also to one of the main reactions of organometallic chemistry—the reaction of metals with halogen derivatives, leading to the formation of a metal–carbon bond. Although this reaction was discovered more than a century ago, the mechanism of the process cannot be considered to be explained. Each of the suggested approaches to the solution of this problem is confirmed by the indirect evidence, but in not one instance is the reasoning conclusive.

Any scheme which pretends to give a rather complete explanation of the nature of this reaction should successfully explain not only the very fact of the formation of a metal–carbon bond but also the nature of the side processes, the effect of the solvent, stereochemical features of the synthesis, etc.

All the points of view on this subject can be roughly divided into two large groups, depending on which of the two species—the radical $R^{\cdot}$ or the carbanion R^{-}—is ascribed the part of "actual start" in the intermediate stage of the reaction.

Suggestions about the free radical nature of the reaction are based mainly on the studies of Polyani and coworkers[183,184], completed as long ago as 1930. The authors studied the reaction of sodium vapour with methyl halides. A kinetically bimolecular reaction leads to the formation of free methyl radicals identified by their reaction with iodine vapour:

$$CH_3X + Na \rightarrow Na^{+}X^{-} + {}^{\cdot}CH_3.$$

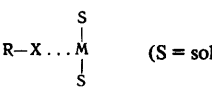
The activation energies fall sharply with decrease in the strength of C–X in the order F ≫ Cl > Br > I.

It is claimed that in a transition state of type $>C\ldots X\ldots M$ transfer of an electron takes place from a metal atom to a chlorine atom, which leads to the production of an ion pair $M^{+}X^{-}$ which is removed from the free radical formed simultaneously.

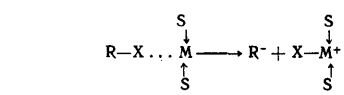
On the other hand, even from the work of Paneth it is well known that free radicals are readily "seated" on the free valencies of the metal with the formation of organometallic compounds[185,186]. Even a simple comparison of these two factors leads to the hypothesis of the free radical nature of the whole process: in the adsorbed layer on the metal surface (according to Polyani's scheme) free radicals are generated, which, by reacting with this surface, also form metal–carbon bonds. In this instance when the chemisorption is insufficient the possibility appears of the escape of the free radicals into the solution with all the consequences that follow: recombination (dimeric products, R–R), disproportionation (mixture of hydrocarbons RH and R_{-H}), interaction with the medium (hydrocarbons RH). On the basis of the extremely approximate kinetic results about the reaction of magnesium with alkyl halides[187,188] even the assumption about a radical-chain mechanism was advanced, which agrees with the existence of an induction period, the acceleration of certain reactions when irradiated, etc.

Another viewpoint mainly being developed by the French school (Prevost[189], Normant[190], and others) is that during the course of organometallic synthesis a carbonion R^{-} is formed as the active species.

In this instance the reaction of an alkyl halide with a metal is regarded as the nucleophilic attack of the metal due to the unshared electron pairs of the halogen. In Prevost's opinion[189], such interaction cannot by itself lead to the formation of a carbanion without the participation of an outside donor of electrons, which is the solvent. The common attack of the halogen and solvent leads to the removal of a metal atom from the lattice and the formation of a hypothetical species of the type:


(S = solvent, M = divalent metal)

which then undergoes intramolecular electron transfer:



The carbanion which is formed either adds to a positively charged metal atom (normal reaction), or participates in the formation of side products:

$$R^{-} + RX \rightarrow R{-}R + X^{-}$$

$$R^{-} + RX \rightarrow RH + R_{-H} + X^{-}.$$

It would appear that a single answer about the validity of one or another of the schemes given above can be given by a study of the stereochemistry of the replacement of a halogen connected to an asymmetric carbon atom by a metal. However, the available results on this seem contradictory. Moreover, the interpretation of any stereochemical results is hindered in this instance by the impossibility of the unambiguous assignment of this reaction to any of the accepted types of substitution. The stereochemistry of redox substitutions has not yet been studied systematically and a basis for the prediction of the stereochemical results of such reactions is still impossible.

The available facts lead to the following results. The stereoisomeric *cis-trans*-halides of the propenyl and stilbenyl types react with lithium, almost completely retaining

the configuration of the sp^2-carbon atom, which is also retained in subsequent reactions for the transfer of an unsaturated radical[191,192].

The stereochemical "purity" of the reaction of *trans*-β-bromostyrene with magnesium depends somewhat on the solvent[193]; however, here also it is possible to speak about retention of configuration.

The substitution of a metal for a halogen connected to a saturated sp^3-carbon atom is less stereospecific on the whole. Optically active organo-magnesium[195] and -lithium[194] compounds are obtained from (+)-(*S*)-1-halogeno-1-methyl-2,2-diphenylcyclopropane; however, most optically active halides of the type RR'R"CX,[196] for example, (−)-3,3-dimethylcyclohexyl chloride[197], form racemic organometallic compounds.

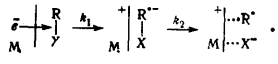
In the reaction of a series of optically active halides with metallic sodium (Wurtz reaction) the optical activity is partly retained[198].

Strictly speaking, all these results do not prove and do not rule out any of the proposed schemes. In particular the retention of the configuration can result both from the formation of "intimate radical pairs" of the



type, where there is no free rotation[194] and from the similarly constructed ion pairs formed by the carbanion and metal ion which are produced.

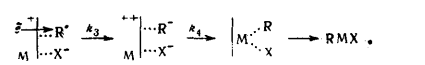
It should be borne in mind that the two main approaches to understanding the mechanism of the RX + M reactions are not mutually exclusive. In any case the first act of this redox reaction taking place on the metal surface must be considered the transfer of "dead" electrons of the metal lattice to the adsorbed molecule of halogen and the formation of the corresponding AR§, $RX^{\cdot -}$,[199] after which there is the breaking of the C–Hal bond and the formation of an organic radical and a halide anion adsorbed on the metal surface:



Depending on the nature of the metal, the organic halide, and the solvent, the breaking of the C–Hal bond can also proceed synchronously with the electron transfer ($k_2 > k_1$). In the last instance the elementary act can be regarded as the nucleophilic attack on the halide adsorbed on the metal surface by an electron (type S_N2)

$$\bar{e} + RX \longrightarrow \bar{e} \ldots R^{\delta+} \ldots X^{\delta-} \longrightarrow R^{\cdot} + X^{-}.$$

The radical which has been formed takes a second electron, being converted into a carbanion, and simultaneously the metal cation enters the solution:



The medium has an enormous influence on the occurrence of all the stages of this process. Firstly, the solvent facilitates the transfer of the electron both on account of the solvation of the cationic centres on the metal and also owing to its own affinity for an electron, which makes possible the transfer of an electron from the metal to the halogen through the solvent¶. Secondly, donor solvents facilitate the stabilisation of AR, $RX^{\cdot -}$, and finally they facilitate, owing to the solvation, the escape of a metal cation into the solution. Catalytic additions evidently usually act similarly.

As regards the mechanism of formation of the side-products (R–R, RH, R_{-H}), two completely different processes must be distinguished: the formation of side-products during the synthesis of an organometallic compound and their formation due to secondary reactions of the metal alkyl already formed. The second type of reaction will be considered in the section dealing with substitutions.

If the rate of conversion of a radical R' into a carbanion is low in comparison with its rate of formation (k_1 and $k_2 > k_3$), there is some probability of its recombination with another of the same radicals on the metal surface (formation of R–R hydrocarbon) or of its escape into the solution (hydrocarbons RH and R_{-H}). A certain amount of side-products can arise due to the reaction of the described carbonium ion R^- with the solvent or form an excess of unreacted halogen derivative:

$$R^- + H^+ \quad \text{(from solvent)} \longrightarrow RH$$
$$R^- + RX \longrightarrow R{-}R + RH + R_{-H} + X^-.$$

If the rate of addition of the second electron is greater than the rate of splitting of the C–Hal–($k_3 > k_2$), the carbanion formed should retain the geometric configuration of the initial halogen derivative. Naturally, this condition can be fulfilled for the more active metals and halogen derivatives, the molecules of which contain atoms and groups of atoms capable of delocalisation of the unpaired electron in RX^-. Actually, optically active organometallic compounds of lithium and magnesium could be obtained only from (+)-(*S*)-1-halogeno-1-methyl-2,2-diphenylcyclopropane, and in the formation of the organomagnesium compound the degree of racemisation is significantly greater[194,195].

If the metal taking part in the reaction is incapable of forming a normal organometallic compound the process stops at the stage of formation of a radical which subsequently either dimerises or disproportionates. Such a direction of the reaction is brought about by the reaction of halogen derivatives with metal derivatives[200].

2. Substitutions

The ability of the anions to act as active electron donors suggests that in many instances the reaction of anions proceeds in stages, the first stage being the transfer of an electron from the anion to the acceptor. Indirect confirmation of this hypothesis is the linear relation between the rate of reaction of the anion (nucleophilic nature) and the half-wave oxidation potential[201–203].

Let us consider, for example, the reaction of anion A^- and cation B^+. Because of the difference in electron affinity of A^- and B^+ (which is completely natural on taking into account that in many reactions the anions act as donors and the cations as acceptors of electrons), the first act is the transfer of an electron from anion to cation with the formation of two radicals, the recombination of which leads to a product corresponding to the normal heterolytic process:

$$A^- + B^+ \xrightarrow{k_1} A^{\cdot} + B^{\cdot} \xrightarrow{k_2} A{-}B.$$

The recombination and disproportionation of like radicals and their interaction with the medium leads to the formation of side-products. Since the recombination of radicals (k_2) usually proceeds at an extremely high rate the observation of valence-unsaturated intermediate species is

§ For the principal possibility of the existence of AR of this type, see p.956.

¶ This assumption is based on the solubility of a series of active metals in amines, esters, and other aprotic solvents[49–54].

possible only when there is a rather large difference in the electron affinities of the initial reagents, that is, when the rate of electron transfer is rather high and is not the rate-limiting stage of the process ($k_1 > k_2$).

In some instances only one of the radicals can be observed (A˙ or B˙) which exhibits relative stability, when the second radical similarly simultaneously participates in some side-process. Finally, there can be the example when the radicals formed are incapable of further changes, that is, the reaction stops at the stage of electron transfer.

Similar discussions can also be held for the reactions of anions (and cations) with neutral molecules (reactions of the ion–dipole type) and for reactions between neutral molecules (reactions of the dipole–dipole type). In the last example the complete transfer of an electron evidently takes place relatively rarely in media of high solvating ability. In many instances some displacement of the electron density takes place with formation of a charge-transfer complex (CTC)†.

Evidently the first experimental confirmation of the formation of radical species in reactions between neutral molecules was obtained in 1958 [7] in an EPR study of the reaction of chlorotriphenylmethane with ethyl-lithium. The concentration of the triphenylmethyl radical under the conditions of the experiment considerably exceeded the equilibrium value which was convincing proof of its primary nature:

$$Ph_3CCl + EtLi \longrightarrow Ph_3C^{\cdot} + LiCl + Et^{\cdot},$$
$$2\,Ph_3C^{\cdot} \longrightarrow Ph_3CCPh_3\ .$$

In addition the results obtained did not solve the problem of the participation of the triphenyl radical in the normal substitution since the reaction products were not studied.

In investigating the reaction of benzophenone with various alkyl- and aryl-magnesium halides the formation of benzophenone ketyl was observed[76]. However, in this instance the results obtained did not permit a definite conclusion to be drawn about the role of electron transfer in normal additions.

In studying the reactions of *p*-nitrobenzyl chloride and *p*-nitrocumyl chloride with various anions (the anion of 2-nitropropane, 2-ethoxycarbonylcoumaran-3-one, the thiophenolate ion), Kornblum and coworkers[205-208] noted the formation of paramagnetic species, which, in their opinion, are the AR of *p*-nitrobenzyl chloride or *p*-nitrocumyl chloride. However, since the authors did not obtain a resolved EPR spectrum, this assumption also cannot be considered completely proved.

Nevertheless, this assumption is indirectly confirmed by the fact that the substitution is retarded by *p*-dinitrobenzene and molecular oxygen.

The present authors with Bubnov recently showed that the alcoholysis of triphenylmethyl chloride and perchlorate with potassium t-butoxide proceeds through a stage of electron transfer[209]. On mixing solutions of triphenylmethyl chloride (or triphenylmethyl perchlorate) with a solution of potassium t-butoxide in the microwave cavity of an EPR spectrometer a well resolved signal of the triphenylmethyl radical was observed, the concentration of which passes through a maximum during the course of the reaction. If potassium 2,4,6-tri-t-butylphenoxide is taken instead of potassium t-butoxide, the reaction stops at the stage of single-electron transfer, since the triphenylmethyl and 2,4,6-tri-t-butylphenoxyl radicals which are formed do not recombine with one another. Measurement of the concentration of phenoxyl radical shows that this process takes place quantitatively. These results show that the classical, as it were, S_N1 reaction is in reality at least a two-stage process: electron transfer and the subsequent recombination of two radicals.

Electron transfer processes evidently also play an important part in nucleophilic substitutions in the aromatic series. It was shown recently[210] that the reaction of esters of *p*-nitrophenol with alkoxides take place through the formation of the corresponding AR.

Despite the fact that electron transfer in substitutions has at present been proved only in isolated instances we consider that this process is extremely general and the lack of direct experimental confirmation is determined by technical difficulties.

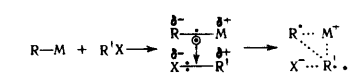
One of the main reactions of organometallic chemistry approaches very closely to the reactions considered: the reaction of organometallic compounds with halogen derivatives. This reaction usually proceeds ambiguously and leads to a complex mixture of products. At least two main directions can be distinguished for this process: double decomposition leading to the formation of a new organo-elemental compound and a halogen derivative.

$$RM + R'X \rightarrow R'M + RX$$

and the Wurtz reaction:

$$RM + R'X \rightarrow R{-}R' + MX\ .$$

The latter is usually complicated by a series of side processes leading to the formation of hydrocarbons of the type RR, R′R′, RH, R_{-H}, R′H, and R'_{-H}. If the Wurtz reaction can be considered as a heterolytic substitution, the exchange reaction cannot be classified as any single type of reaction in accordance with the classification accepted in organic chemistry. Formally, during the course of the reaction there is a conversion of the "carbanion" of the organometallic compound into a "carbonium ion" of the halogen derivative and respectively the "carbonium ion" of the initial halogen derivative into the corresponding "carbanion". Hence it is quite evident that here we are dealing with a redox process. Since in this pair of reagents the donor properties should naturally be exhibited by organometallic compounds (RM), the first act of the reaction should be the transfer of an electron by the metal–carbon bond to the molecule of the halogen derivative:



In the complex which is formed two main directions of the process are subsequently possible: the transfer of a second electron with the formation of a carbanion R′⁻ (exchange reaction) and recombination of the radicals R˙ and R′˙, leading to the products of the Wurtz reaction. As well as these normal processes there is a certain probability of escape of radicals into the solution, which should lead to the formation of side-products—hydrocarbons of the type RH and R_{-H}. Since as a result of the exchange reaction both organometallic compounds (initial and that formed from the added halogen derivative) are always present in the reaction mixture, their reactions with the halides leads to the formation of the so-called "doubled" radicals—RR and R′R′. The ratio of the reaction products in each particular instance depends chiefly on the polarity of the C–M bond, the relative electron affinity of R˙ and R′˙, and the solvating ability of the medium. The higher the polarity of the C–M bond, the easier the electron transfer and the easier the normal reactions (compare the

† See Kosower[204] for the role of CTC in organic reactions.

organolithium and organomagnesium compounds). An increase in the difference in electron affinity of R and R′ facilitates the exchange reaction[211] and simultaneously can lead to a decrease in the yield of the product of the normal Wurtz reaction, if the organometallic compound formed reacts more readily with the initial halogen derivatives[212]. The role of the medium appears, on the one hand, in a change in polarity of the C–M bond and on the other in the solvation of the intermediate reaction complex. The stabilisation of this complex in solvating solvents should lead to an increase in the normal Wurtz and exchange reactions. Actually, many examples[212–214] have shown that a solvating solvent greatly facilitates a Wurtz reaction, whereas homolytic processes predominate in non-solvating media[215,216]. An increase in the solvating ability of the medium leads to a sharp increase in the exchange rate in the series of organolithium[218] and organomagnesium[219] compounds.

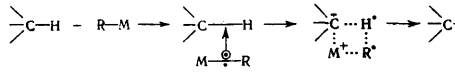
The problem of the catalytic activity of transition metal salts in this reaction is closely connected with the problem under consideration[220]. The role of these catalysts is that they serve as electron transporters, acting as an electron acceptor in relation to the potential carbanion of the organometallic compound. The reduced form of the catalyst then gives the excess electron to a molecule of the organic halide, and evidently such a stepwise electron transfer is hypothetical.

The first stage of this process is effected in the oxidative dimerisation of monosubstituted acetylenes by copper(II) ions in the presence of bases[217]:

$$RC{\equiv}C^- + Cu^{2+} \rightarrow RC{\equiv}C^{\cdot} + Cu^+$$
$$2\,RC{\equiv}C^{\cdot} \rightarrow RC{\equiv}C{-}C{\equiv}CR\,.$$

Depending on the nature of the initial reagents and catalyst this transfer can be effected either in a molecular complex[221,222] or both stages can proceed separately, so that the interaction of unlike radicals is hindered or completely impossible, as, for example, occurs in the reaction of alkylmagnesium halides with aryl halides[220]. In this connection it is not surprising that this reaction is catalysed also by certain other electron acceptors, for example, azobenzene[223].

General considerations concerning the mechanism of the RM + RX′ reaction can also be applied to the reactions in the metallation of aromatic hydrocarbons containing "acid" hydrogen atoms. In the reaction complex formed as a result of electron transfer the loss of a hydrogen atom takes place owing to its recombination with a radical from the organometallic compound:

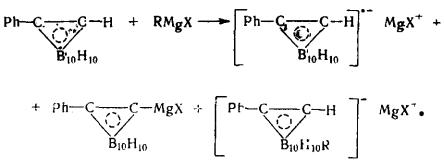


If the AR formed is relatively stable the radical from the organometallic compound can be attached to the aromatic system with formation of the corresponding alkyl derivatives. Actually, in several instances the alkylation of aromatic hydrocarbons under the action of organometallic compounds was observed. Thus in the metallation of perylene, in addition to perylenecarboxylic acid (after carboxylation) 13% 1-butylperylene and a little 3-butylperylene were isolated[224].

Dixon and coworkers[225,226] found that the ease of alkylation increases in the order toluene < benzene < biphenyl < < naphthalene, phenanthrene, but the electron affinity and ability to form AR increase in the same order[41,42]. The ease of alkylation of various organolithium compounds increases in the order n-BuLi < s-BuLi < t-BuLi and as already mentioned above, the ability of the RLi to transfer an electron increases in the same order[91].

A comparison of different RLi by their metallating ability in relation to triphenylmethane[227] and by their donor activity[73] leads to the same sequence: benzyl > allyl > > n-butyl > phenyl > methyl.

The formation of AR, alkylation, and metallation was observed in the reaction of phenylbarene with alkylmagnesium halides[228]:



Of course, it is impossible to regard the examples given as proof of the general scheme of metallation suggested, but the good qualitative agreement with the results of the experiments is indirect evidence in support of the above approach to the mechanism of metallation.

3. Other Reactions

First of all among the electron transfer reactions should be put the oxidation of organic compounds, but the number of experimental studies confirming this viewpoint are extremely few.

Russel and coworkers[229], in studying the oxidation of carbanions by oxygen, concluded that this reaction best agrees with the electron transfer scheme:

$$R^- + O_2 \rightarrow R^{\cdot} + O_2^{\cdot-}.$$

Several articles by Dewar and coworkers[230–232] on the oxidation of various aromatic esters by manganese(III) acetate appeared recently. The kinetic results suggest that in the systems studied the oxidation proceeds through a reversible stage of an single-electron transfer. Analogous results were obtained in investigating the kinetics of the oxidation of a series of the simplest amines by chlorine dioxide[233].

Direct experimental confirmation of electron transfer during oxidation was obtained by Smentowski[234], who observed the formation of AR by nitrobenzene in the oxidation of thiophenoxides by nitrobenzene:

$$ArS^- + PhNO \rightarrow \underset{\downarrow}{ArS^{\cdot}} + PhNO^{\cdot-} \rightarrow \text{reduction products}\,.$$
$$ArSSAr$$

Maruyama[235] noted the formation of diphenylnitrogen oxide in the reaction of phenylmagnesium bromide with nitrobenzene. Evidently in the reaction the diphenylhydroxylaminium anion formed is oxidised by the excess of nitrobenzene:

$$PhNO + PhMgX \rightarrow Ph_2NOMgX \xrightarrow{PhNO} Ph_2N{-}O^{\cdot} + PhNO^{\cdot-}.$$

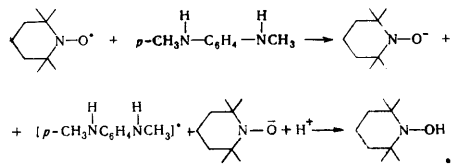
Similarly, the formation of di-t-butyl-[236] and t-butylphenylnitrogen oxide[237] probably occurs in the reaction of t-nitrobutane with t-butylmagnesium chloride and phenylmagnesium bromide.

The formation of the CR of tetramethylhydrazine was noted in the reaction of tetramethyltetrazine with various anhydrides of carboxylic acids[238]:

$$(CH_3)_2NN{=}NN(CH_3)_2 \xrightarrow[0^\circ]{Ac_2O} N_2 + [(CH_3)_2NN(CH_3)_2]^{\cdot+}.$$

Interesting results were obtained in investigating the reaction of stable nitrosyl radicals with aromatic amines.

It was found that the formation of hydroxylamine is a two-stage process: electron transfer from the aromatic amine and addition of a proton from the solvent[239]. In this the aromatic amine is converted into the corresponding CR:



Finally, there are results on the important role of electron transfer reactions in the isomerisation of tetraphenylbutadiene[240], Friedel–Crafts alkylation[241], the diene synthesis[242], and several other processes.

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The subject under discussion is extremely general in character since it evidently touches all the fields of organic chemistry to some extent. Therefore an exhaustive treatment of single-electron transfer reactions would scarcely be possible within the framework of a single review.

Nevertheless the material presented shows that electron transfer reactions play an important part in the elementary acts of many organic reactions. The transference ideas about the electron, both about the kinetic particle widely distributed in inorganic and radiation chemistry, into organic chemistry allows the mechanism of organic reactions which do not fit within the framework of classical theory to be explained in many instances (for example, it allows the simultaneous occurrence of homolytic and heterolytic processes to be explained from a single standpoint).

The fruitfulness of such an approach is also confirmed by the fact that the number of publications devoted to electron transfer reactions in organic chemistry has grown sharply recently. The further accumulation of experimental results in this field will undoubtedly lead to an extension of our knowledge about the nature of chemical changes.

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