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ION-RADICAL ORGANIC REACTIONS

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CONTENTS

I. INTRODUCTION

Contemporary-day organic chemistry trends are towards investigations into the structure and reactivity of intermediate particles originating on the pathway from the starting compounds to the end products. Knowledge of properties of the intermediate particles and penetration into the mechanism of reactions open up new venues towards increasing the rate of formation and the yield of the desired final products. Up to quite recently, chemists focused their attention on radicals or charged particles of the carbanion (carbenium cation) type. Particles of an intermediate nature combining the ionic and the radical properties—the ion-radicals—remained outside the scope of their investigations. Perfected instrumental techniques markedly advanced fine experiments. As a corollary, particles which were little, if at all, known to chemists of previous decades now came to the forefront.

This review has two sections. The first considers the identification of ion-radical reactions and the second treats their optimization. The aim of the investigation is to determine whether the reaction proceeds through the formation of ion-radicals and, if so, which radicals originate and at what stages, and whether these stages belong to the main or side routes of the reaction. Means of revealing ion-radical conversions include physical methods, kinetic data and, finally, purely chemical information on the nature of end products. In this review we had to weave together these methods to form a cohesive unit. In order to help the reader understand the essence of one or another method we consider them separately and then illustrate the complex approach to the solution of the problem by several examples.

As is quite evident, ion-radical conversions need special approaches to initiate or inhibit them. This follows from the peculiar properties of ion-radicals. Ion-radical reactions may be initiated by creating conditions promoting the initial stage of the reaction—namely one-electron transfer. Many ion-radical syntheses are highly selective, yielding products unattainable by other methods or under such mild

conditions. The aim of the second part of the review is to analyze the phenomena which underlie the optimization of ion-radical reactions.

II. IDENTIFICATION OF ION-RADICAL REACTIONS

1. *Structure of final products*

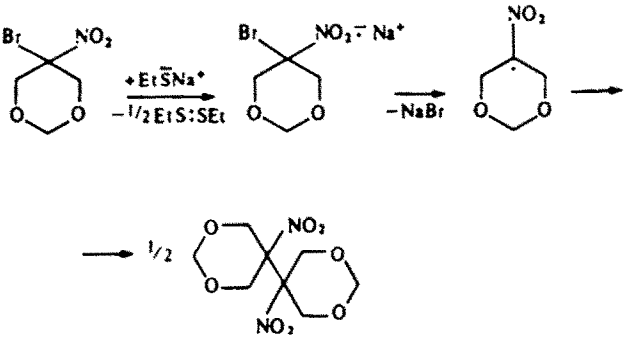
The interaction of alkyl halides and mercaptans or alkaline mercaptides produces thioalkyl derivatives. This is a typical nucleophilic substitution reaction, and one cannot tell by the nature of products whether it proceeds through the ion-radical stage or not. However, the version of the reaction given in Scheme 1 may be explained only by the intermediate stage involving electron transfer. As has been found,[1] 5-bromo-5-nitro-1,3-dioxane reacting with an equimolar amount of sodium ethylmercaptide in DMSO at 20° under argon yields after 3 hr 5,5'-bis(5-nitro-1,3-dioxanyl) (yield 90%), diethyldisulphide (yield 95%) and sodium bromide (quantitative yield). UV-irradiation markedly accelerates the reaction (5-bromo-5-nitro-1,3-dioxane completely converts in 15–20 min), while benzene nitro derivatives decelerate it.

The results obtained show that the process begins with the formation of ethylthiyl radicals and anion-radicals of the substrate. Ethylthiyl radicals dimerize (diethyldisulphide is obtained) and anion-radicals of the substrate decompose monomolecularly to give 5-nitro-1,3-dioxa-5-cyclohexyl radicals. The latter recombine and form the end dioxanyl.

The thioarylation of 9-bromo-9-phenylfluorene[2] proceeds in a similar way. This example clearly illustrates what makes the ion-radical mechanism so essential.

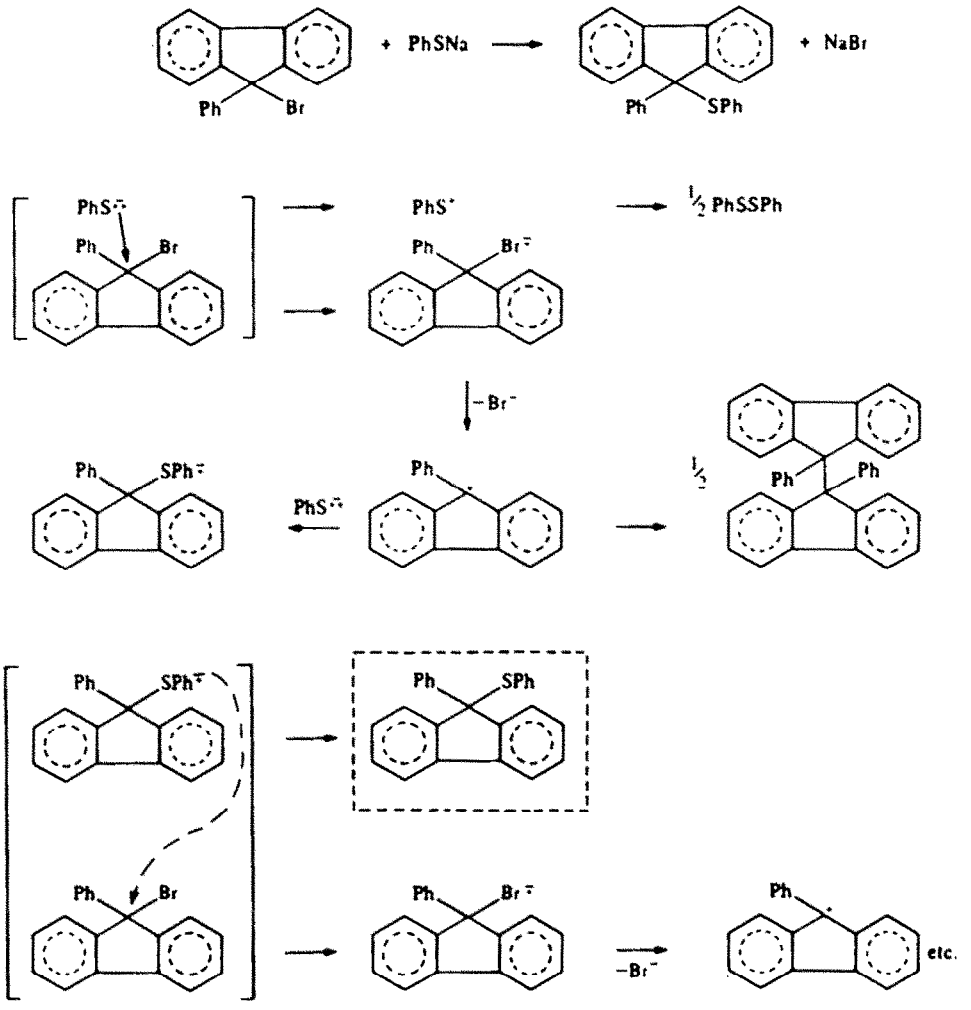
Reaction of 9-bromo-9-phenylfluorene and sodium thiophenolate in DMF under nitrogen (30°, 4 hr) gives sodium bromide and 9-phenylthio-9-phenylfluorene (Scheme 2). Sodium bromide is produced in the quantitative yield but the yield of the product of the nucleophilic substitution is only 42%. The substrate and the nucleophile also enter into other conversions leading to 9,9-diphenylbifluorenyl (yield 33%) and diphenyldisulphide (yield 30%). The formation of these substances contradicts common ideas on nucleophilic substitution. The presence of radical traps (oxygen or tetrabromobenzoquinone), and this is especially important, decelerates the formation of both unexpected compounds and the product of thioarylation. Thus, the stage of the electron transfer from the nucleophile to the substrate lies on the main pathway of the reaction; this stage produces the phenylthiyl radical and the anion-radical of the substrate. Both radical products undergo further conversions: the phenylthiyl radical gives diphenyldisulphide and the anion-radical of the substrate produces the 9-fluorenyl radical. The latter reacts in two directions. Dimerizing it forms bifluorenyl and reacting with the nucleophile it gives the anion-radical of the nucleophilic substitution product. The chain continues because the electron from the anion-radical is transferred to the unreacted molecule of the substrate which loses bromine and then reacts with the nucleophile and so on.

The mechanism of the reaction given in Scheme 2 differs from the S_N1 or S_N2 mechanism in that it involves the stage of one-electron oxidation–reduction.† The driving force of this stage may be an easy cleavage of the bromine anion followed by the formation of the fluorenyl radical. The latter is unsaturated at position 9 near three benzene nuclei which stabilize the radical centre.



Scheme 1.

† The mechanism is designated $S_{RN}1$. This means substitution radical, nucleophilic, monomolecular.

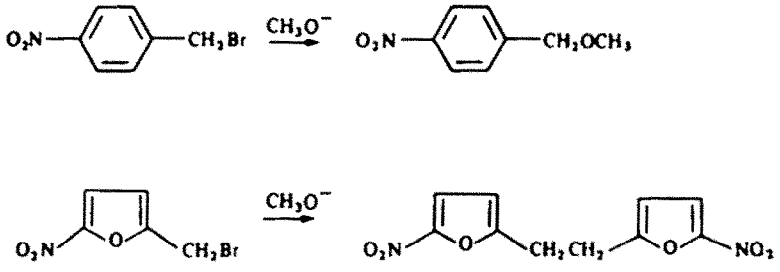


Scheme 2.

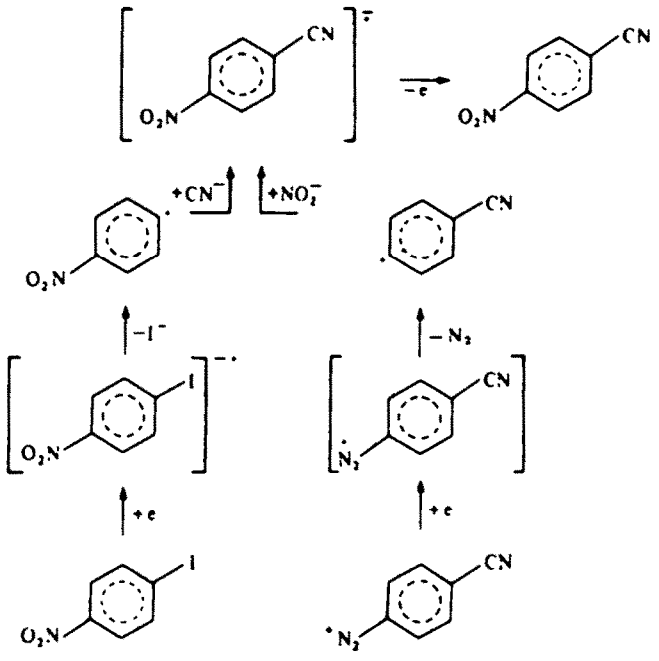
Even in one series, different derivatives can react differently with one and the same nucleophile. Thus, 4-nitrobenzyl bromide and 5-nitrofurfuryl bromide subjected to the action of sodium methylate in methyl alcohol produce, respectively: methyl-4-nitrobenzyl ester and 1,2-bis(5-nitro-2-furyl)ethane converting to the corresponding ethylene under the conditions of the reaction.[3] The difference is quite evident from Scheme 3. The author[3] thinks that different electron-acceptor properties of the substrates determine the S_N2 or electron transfer pathways of the reaction.

It is of interest that the substrates shown in Scheme 3 react similarly with the cyanide ion producing the corresponding ethanes.[3]

Russell[4] reconstructed the stage of the nucleophilic substitution of 4-iodonitrobenzene with the cyanide ion. One-electron reduction at the cathode in the presence of cyanide leads to the anion-radical



Scheme 3.



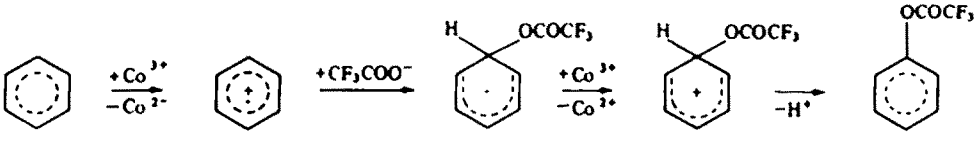
Scheme 4.

of 4-iodonitrobenzene (Scheme 4). Like other halide derivatives, 4-iodonitrobenzene in the anion-radical state easily cleaves the halide anion and converts it into the 4-nitrophenyl radical. The latter reacts with the cyanide ion and produces the anion-radical of 4-cyanonitrobenzene. The ion-radical may be obtained by reducing the 4-cyanobenzenediazonium salt with dithionite in the presence of nitrite. One-electron oxidation with the initial substrate converts the anion-radical into the neutral 4-cyanonitrobenzene (Scheme 4).

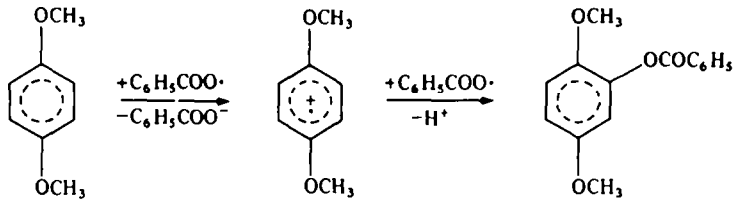
The acetoxylation of the aromatic compounds, chemical or at the anode, produces similar results. Kochi *et al.*[5] found a way of stabilizing the cation-radical in trifluoroacetic acid. The method involves rapid mixing of the solutions of the aromatic compound and trifluoroacetates of three valence thallium and cobalt, and their freezing. During defreezing the samples give well resolved spectra of the aromatic cation-radicals. The latter convert into the arylic esters of trifluoroacetic acid. One molecule of the aromatic compound consumes two molecules of the oxidizer;[5] the limiting stage of the reaction is one-electron oxidation producing the cation-radical. Scheme 5 visualizes the described conversions for benzene.

The anodic acetoxylation of the aromatic compounds in the solutions of acetic acid carrying alkali metal or tetraalkylammonium acetates takes the same route. As the investigations[6,7] have shown, the process starts with one-electron oxidation at the anode and then passes through the same stages as in Scheme 5. The reaction takes place at potentials sufficient to oxidize the substrate but not sufficient to convert the acetate ion into the acetoxy radical. The acetoxy group comes to the product not from acetic acid (solvent) but from the acetate ion (conducting electrolyte):[6] salts with tosylate or perchlorate anions stop the acetoxylation in the solution of acetic acid.

Radical substitution may also proceed through the cation-radical stage. The monograph[8] discusses the introduction of the benzoyloxy group into the aromatic nucleus. Thus, benzoyl peroxide interacting with the benzene derivatives bearing electron-donor substituents yields the products of hydrogen replacement by the benzoyloxy group. When the nulceus carries the electron-acceptor



Scheme 5.



Scheme 6.

substituents, diaryls form; in other words, only the phenylation takes place. This may be explained by electron transfer from the aromatic substrate to the benzoyloxy radical. As follows from Scheme 6, one-electron oxidation of 1,4-dimethoxybenzene produces the cation-radical. The cation-radical, being more active than the initial substrate, recombines with the benzoyloxy radical before the latter decomposes into the phenyl radical and carbon dioxide. The process ends with the formation of a stable substitution product (Scheme 6).

In the case of anisole the reaction takes the route shown in Scheme 7. The reaction yields only products of the *ortho*- and *para*-substitution, the *meta*-isomer is lacking. If it were a standard radical substitution reaction, the *meta*-isomer should obviously be formed in a certain amount.

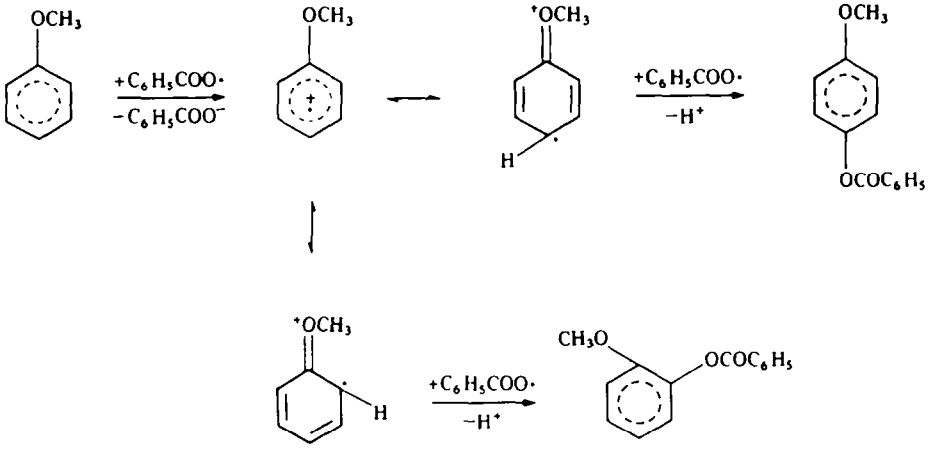
Schemes 6 and 7 show that the introduction of the electron-acceptor substituents enhances the stability of the substrate to oxidation and prevents electron transfer to the benzoyloxy radical. As a result, the phenylation takes place instead of the benzoyloxylation, and the phenyl radical enters into any free position.

Analyzing the structure of the end products, we can tell whether the reaction had the ion-radical mechanism or not. To this end, not only the main but also the side or secondary reaction products should be subjected to analysis. The reaction, however, may yield only a sole product. And though the reaction took the ion-radical pathway, the end product may not differ from the product anticipated from the ordinary reaction.

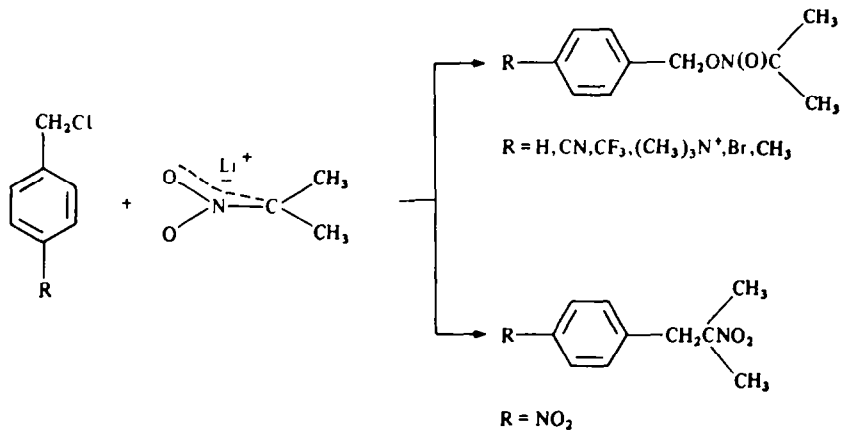
2. *Changing the direction of reaction. Violation of σ,ρ-correlations when passing from standard to ion-radical mechanism*

σ,ρ-Analysis of a broad range of organic reactions has demonstrated that within the framework of one mechanism a definite characteristic of a reaction centre linearly depends on the constants of substituents acting on the centre. When the linear correlation is disturbed, or the slope of the σ–ρ curve changes, or the reaction takes another route, this means that compounds participating in the reaction react by another mechanism.

We shall illustrate this on several examples. While interacting with the anion of 2-nitropropane, benzyl chloride and its derivatives bearing groups CN, CF_3, $(CH_3)_2N^+$, CH_3 and Br in the *para*-position yield products of O-alkylation.[9] However, when the nitro group takes the place of the above



Scheme 7.



Scheme 8.

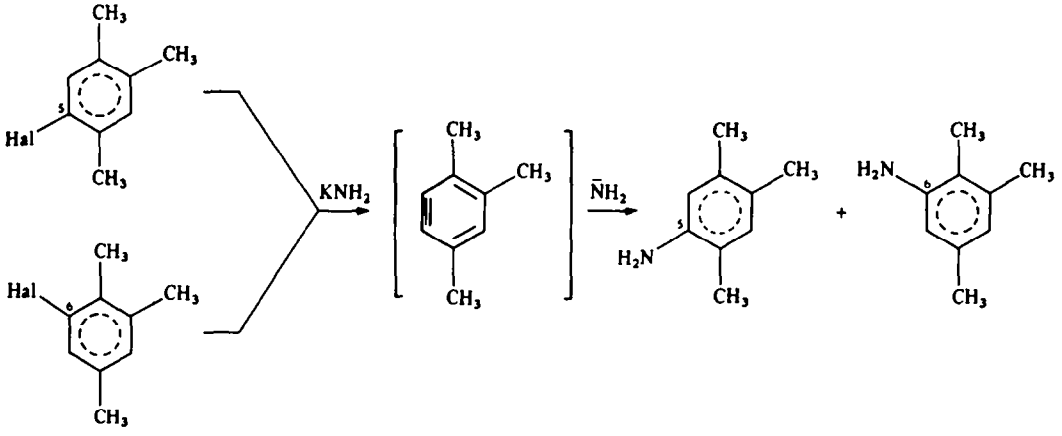
substituents, the reaction gives the products of C-alkylation[9] (Scheme 8). When the substituent is the nitro group, the anion-radicals are more easily produced, they are more stable, and the reaction takes the ion-radical pathway.

Kim and Bunnett[10] have demonstrated in a similar way that the substitution of the amino group for iodine in iodotrimethylbenzene proceeds by the ion-radical mechanism as a contrast to the bromo- and chloro-analogues. The reaction of 5- and 6-pseudocumenes with potassium amide in liquid ammonia gives 5- and 6-pseudocumidines; this is the cine-substitution reaction (Scheme 9). As the scheme shows, the reaction yields both isomeric amines irrespective of the halide position (5 or 6) in the initial molecule. In the case of chloro- and bromo-analogues the ratio of 5- and 6-amino-derivatives is independent of halide and is always close to one and a half. The reactions proceed according to the same mechanism. For analogues bearing iodine the ratio changes. It decreases to 0.63 in the case of 5-iodopseudocumene and rises to 5.86 in the case of 6-iodopseudocumene. This means that iodo-derivatives react not only by the mechanism of cine-substitution but also by another mechanism, the contribution of which differs for the 5- and 6-isomers.

Iodo-derivatives, however, produce amino-derivatives in the ratio one and a half if the reaction is conducted in the presence of tertbutylnitroxide or tetraphenylhydrazine.[10] Because these agents absorb radicals authors conclude that iodo-derivatives may react by the mechanism of cine-substitution and at the same time by the ion-radical mechanism shown in Scheme 10.

Ion-radicals of iodopseudocumene cleave the halide-anion more easily than bromo- and chloro-analogues. This makes pathway 10 involving electron transfer essential.

The ion-radical pathway of the reaction sometimes reflects in changes of the coefficient ρ in the relationship connecting the substituent constants and the reaction rates. This may sometimes be used when determining the mechanism of the reaction. Now we shall illustrate this. The rate of formation of



Scheme 9.

$$ArJ \longrightarrow (ArJ)^{\cdot -} \longrightarrow Ar^{\cdot} + J^{-};$$

$$Ar^{\cdot} + NH_2^{-} \longrightarrow (ArNH_2)^{\cdot -};$$

$$(ArNH_2)^{\cdot -} + ArJ \longrightarrow \boxed{ArNH_2} + (ArJ)^{\cdot -} \text{ etc.}$$

Scheme 10.

aryl iodides from aryl diazonium salts and potassium iodide in methyl alcohol depends on the nature of the substituent conjugated with the diazo group.[11] Electron-donor substituents decelerate the process as compared with benzene diazonium (the substituent is hydrogen), whereas electron-acceptor substituents accelerate it. Oxygen inhibits the reaction and photoirradiation speeds it up. As has been reported,[11] in the case of 4-nitrobenzene diazonium, the reaction produces not only 4-iodonitrobenzene but also nitrobenzene, elemental iodine and formaldehyde. All this supports the mechanism presented in Scheme 11.

The nitrophenyl radical may react with the iodo-ion and the solvent, methyl alcohol. The transference of the hydrogen radical from methyl alcohol to the nitrophenyl radical yields nitrobenzene and formaldehyde ($CH_3OH \rightarrow CH_2O$). Though carefully sought among the products of the reaction, 3-iodonitrobenzene and 4-nitroanisole were lacking. This completely rejects another possible mechanism of the reaction, that is cine-substitution, which involves the formation of dehydrobenzene (Scheme 9).

3. *Leaving group strength*

Standard nucleophilic substitutions show a clear-cut dependence between the rate of the process and the strength of the leaving group. The residue of piperidine replaces a substituent in a series of 4-substituted nitrobenzenes with the following relative rates (DMSO, 50°): 1 (Cl), 412 (F), 1.17 (Br), 0.26 (J), 0.01 (SC_6H_5).[12] Similar reactions of amination proceed in liquid ammonia at photostimulation but the above sequence is disturbed. Bunnett[13] supports the ion-radical mechanism of the reaction and shows that similar doses of irradiation make iodides more active than bromides, while chlorides and fluorides react with great difficulty, if at all. The photostimulated reaction of aryl halides with sodium thiophenolate (liquid ammonia, −45°) shows that aryl iodides undergo substitution, aryl chlorides probably do not react, and an aryl bromide was obtained only in a single case (the yield of Ph_2S is about 20%).[14] It is of interest that triethylamine and tetrabutylammonium hydroxide facilitate substitution and PhSNa produces diphenyl sulphide when acting both on bromobenzene (yield 65–70%) and on chlorobenzene (yield 30–33%).[15] The catalysts probably act as additional electron donors and initiate the formation of the primary anion-radical of the substrate. The anion-radical may originate in the donor–acceptor complex, the substrate-nitrous base. This should also promote the decomposition of the anion-radical under photoirradiation.

Thus, the violation of the correlation between the ease of the reaction and the strength of leaving groups definitely supports the ion-radical mechanism of the reaction. This, however, cannot be sufficient proof because, as discussed in Section II-2, cine-substitution producing arynes also disturbs a common correlation. Besides, it should be noted that the $S_{RN}1$ mechanism does not assign the main part in the reaction to the leaving group X^- in $ArX^{\cdot -}$. The nature of X affects only the rate of fragmentation $ArX^{\cdot -} \rightarrow Ar^{\cdot} + X^-$. And indeed, the rate of fragmentation of the anion-radicals increases in the series, F, Cl, Br, J.[16] If we provide a strong energy pumping, say, increase the dose of irradiation, the rates of fragmentation will equalize. The capture of $Ar^{\cdot}$ by a nucleophile will become a limiting stage and it cannot depend on the nature of a leaving group. In fact, the reactivities of phenyl iodide, phenyl bromide, phenyl chloride, phenyl fluoride, phenyltrimethylammonium iodide and diphenyl sulphide towards a pair of nucleophiles $(EtO)_2PO\ K^+$(P) and t-BuC(O)$CH_2^-K^+$(C) under conditions of

$$Ar{-}N_2^+ + J^- \longrightarrow ArN_2^{\cdot} + J^{\cdot};\ J^{\cdot} \longrightarrow 1/2J_2;$$

$$ArN_2^{\cdot} \xrightarrow{-N_2} Ar^{\cdot};\ Ar^{\cdot} + J^- \longrightarrow Ar{-}J^{\cdot -}$$

$$Ar{-}J^{\cdot -} + ArN_2^+ \longrightarrow \boxed{ArJ} + ArN_2^{\cdot} \text{ etc.}$$

Scheme 11.

sufficient irradiation are very close. For all substrates k_P/k_C (liquid ammonia, N_2 atmosphere, $-40°$) is equal on average to 1.4; the deviation does not exceed 8–10%;[17] k_P is the rate constant for the reaction with P [$(EtO)_2POK$] and k_C is the same constant with C [$tBuC(O)CH_2K$].

4. *Kinetic isotopic effects*

As is well known, the rate constant of a reaction changes when the atom participating in the reaction is replaced by an isotope. Deuterium and tritium are the most commonly used isotopes. The quantitative measure of the kinetic isotopic effect is the ratio of the reaction rate constants, for example k_H/k_D. The greatest isotopic effect is observed in the case of a hydrogen isotope.[18] This effect proves conclusively that a particular atom is subject to attack and that a labelled bond participates in the limiting stage of a complex chemical reaction. The kinetic isotopic effects as applied to the ion-radical reactions have the following peculiarities. The ion-radical reactions presuppose electron transfer from donor to acceptor. An electron leaves the upper occupied orbital belonging to the whole donor molecule and populates the lower vacant orbital of the whole acceptor molecule. This process certainly differs from the substitution of atoms and groups. Thus, the direct connection between the "heavity" of leaving group and the rate of its cleavage cannot be the primary cause of the effect.

Dimethylsulphide accelerates the decomposition of tert-butylperoxybenzoate.[19] Dimethylsulphide acts as a donor, whereas the peroxide is the electron acceptor. The rate of reaction drops one and a half times when the deuteroanalogue $(CD_3)_2S$ is used instead of $(CH_3)_2S$. The deuterated compound has a higher ionization potential (I); ΔI for $(CD_3)_2S$ and $(CH_3)_2S$ is about 230 cal/mol.[19] If we assume that the difference comes out in full in the transition state, the isotopic effect k_H/k_D of the reaction of the electron transfer from dimethylsulphide to tert-butylperoxybenzoate should be 1.4 at 80°. This is close to the reported value.[19]

From a theoretical standpoint, electron transfer is the resonance transition between the vibrational levels of a system comprising reagents and a solvent.[20] The reagents and products have approximately the single frequency of intramolecular vibration and the single ionization potential. Their interaction with a solvent (polar medium) is characterized by the frequency of the reagent or product molecule vibrations inside the ionic shell and the polar medium itself is characterized by energy (E_S) showing a change in its polarization at electron transfer. At a constant E_S the probability of electron transfer is greater when $\Delta I < E_S$ and lower when $\Delta I > E_S$. It is quite clear that a pronounced isotopic effect is observed only when $\Delta I > E_S$. This is true only when $\Delta I > 0$.

Because the reactions of electron transfer proceed through a polar transition state, k_H/k_D depends above all on the dielectric constant of a solvent. This peculiarity of the kinetic isotopic effect is used to establish the ion-radical stage in reactions of phenylhydrazones with quinones (solvents dimethylsulphoxide, acetonitrile, tetrahydrofuran, dioxane).[21]

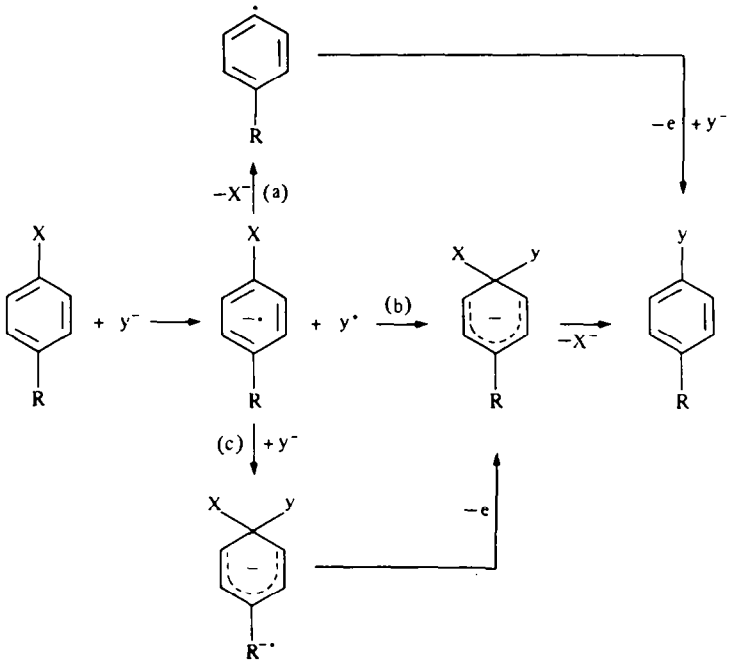
5. *Kinetic approaches*

A thorough investigation into the kinetics of a chemical reaction usually, although not always, establishes its mechanism. However, it should be borne in mind that the same initial compounds may produce the same end products by different mechanisms. Thus, the ion-radical scheme of aromatic nucleophilic substitutions may cover a whole range of pathways (Scheme 12).[22] As the scheme shows, the conversion of the anion-radical of the substrate may proceed through the radical, through the anionic σ-complex, or through the anion-radical of this σ-complex. The contribution of each mechanism depends on the reaction conditions, the effect of the compound structure and medium included.

As a result, the researchers face the problem of estimating the contribution of one or another mechanism of the reaction and determining the type of intermediate particle. According to Schein[22] the commonly accepted classification of the mechanisms of aromatic nucleophilic substitutions by the reaction order is incomplete. His suggestion is to classify the mechanisms by the type of the intermediate particle: the ion-radical, free radical, carbanionic, etc. Above all, several intermediate particles may participate in the reactions.

To illustrate what has been said above it seems useful to consider any ion-radical reaction thoroughly studied kinetically. Let this reaction be the substitution of the nitro group in *o*-dinitrobenzene (*o*-DNB) by the hydroxy group. The researchers have established that:

(i) *o*-DNB reacting with OH^- in aqueous dimethylsulphoxide produces only *o*-nitrophenolate and nitrite;[23] (ii) mixing of reagents quantitatively yields long-lived anion-radicals of *o*-DNB;[23,24] (iii) ion



Scheme 12.

OH^- is indeed the donor of electrons within the system, and it converts into a short-lived radical $OH^{\cdot}$;[24] (iv) the pathway to *o*-nitrophenolate proceeds through a σ-complex carrying the OH group at a tetrahedral carbon;[23,25] (v) the initial *o*-DNB and the σ-complex do not exchange an electron;[23] (vi) the first stage of electron transfer, yielding the anion-radical, in the interaction of *o*-DNB with OH^- proceeds with the participation of the uncharged *o*-DNB;[23] (vii) the kinetic curve of the accumulation and consumption of the *o*-DNB anion-radicals is S-shaped and that of the accumulation of nitrophenolate is parabolic. The curve of the anion-radical starts to dip at the knee of the curve of the end product;[23] (viii) kinetic calculations accord well with the experimental data when the anion-radical of *o*-DNB is considered as the starting compound in the substitution of OH^- for the nitro group.[23]

The results given above unambiguously support the ion-radical mechanism of the reaction. The anion-radical of *o*-DNB is long-lived and does not decompose into the nitrophenyl radical and nitrite ion. Therefore we may conclude that the radical pathway (Scheme 12a) is not essential. The kinetics of the accumulation and consumption of anion-radicals of the substrate as compared with the kinetics of the product (*o*-nitrophenol) accumulation shows that the anion-radicals leave the cage, pass into the solvent pool, and form the anion-radical of the negatively charged σ-complex (Scheme 12b). The "hidden-radical" pathway producing the anionic σ-complex by the mechanism of bimolecular nucleation (Scheme 12c) coexists with the main route, if at all.

Thus, despite the complexity of the problem, the kinetic approaches make its solution quite possible.

We now turn to the stages of the ion-radical conversion and try to estimate the activation barriers for each of the stages.

The initiation of the ion-radical conversion. In the general case this is the interaction of a donor (D) and an acceptor (A) involving transfer of one electron. The probability of one-electron transfer is determined by thermodynamics, namely the positive difference between the acceptor electron affinity and the donor ionization potential. The electron transfer is accompanied by a change in the solvate surroundings: charged particles form and the solvent molecules (the solvent is usually polar) create a sphere around the particles thereby promoting their formation. Elevated temperatures destroy the solvate shell and hinder the conversion. Besides, electron transfer is often preceded by the formation of the charge transfer complexes by the scheme:

$$D + A \rightarrow D \ldots A \rightarrow [D^{\delta+}, A^{\delta-}] \rightarrow [D^{+\cdot}, A^{-\cdot}] \rightarrow D^{+\cdot} + A^{-\cdot}.$$

$$(Ph_2C{=}CPh_2)^{-\cdot}K^+ + THF + (Ph_2C{=}CPh_2)^{-\cdot}K^+ \cdot THF \rightleftharpoons$$

$$\rightleftharpoons Ph_2C{=}CPh_2 + (Ph_2C{=}CPh_2)^{2-}2K^+ \cdot THF$$

Scheme 13.

As is quite evident, the formation of the charge transfer complexes presupposes that molecules of donor and acceptor are held in place by some forces. Here too an increase in temperature hinders the production of complexes because it increases the disorder of molecules in the solution. To summarize, the stage of origin of the ion-radical conversion has, as a rule, a negative temperature coefficient or, in any event, does not increase the total activation energy of the ion-radical reaction.

The development of the ion-radical reaction. The possible mechanisms of the ion-radical conversions are shown in Scheme 12; although the scheme represents the anion-radical reactions it can well illustrate the cation-radical conversions proceeding by a similar pattern. So far, the researchers have failed to separate all the directions shown in Scheme 12 and study them kinetically. It is clear, however, that a deep reconstruction of a molecule associated with the bond cleavage cannot take place at a negative or zero activation energy. Thus, the decomposition of 4-iodo- and 4-bromonitrobenzenes in acetonitrile and dimethylformamide

$$ArX^{-\cdot} \rightarrow Ar^{\cdot} + X^-$$

has a positive activation energy (17–20 kcal/mol).[26] However, the reaction of the phenyl radical with the iodide ion

$$Ph^{\cdot} + I^- \rightarrow PhI^{-\cdot}$$

depends only on the number of collisions of the particles and has a zero activation energy.[27] The nonempirical calculation of the total potential profile of the reaction of radicals $^{\cdot}CH_2NO_2$ with anions $-CH_2NO_2$ also gives zero activation energy, and this accords well with the results of experiment.[28] The interaction of the ion-radicals with the initial neutral molecules[28] or radicals[29,30] also proceeds with zero activation energy.

Therefore it may be concluded that ion-radical reactions have, in general, only a moderately great activation energy and, if permitted thermodynamically, proceed under sufficiently mild conditions.

Now we must focus our attention on a practically important group of ion-radical reactions, i.e. recombinations. They may proceed either as disproportionation or as dimerization. It is of interest to compare this type of recombination with the recombination of radicals. As is known, the radicals interact at zero activation energy. Ion-radicals have a dual nature: as radicals they are highly reactive and as ions they attract particles of an opposite charge and repel those of the same charge. A disproportionation is the interaction of ion-radicals of equal signs. As a rule, the driving force of the ion-radical disproportionation consists of resolvation producing more stable aggregates. For example, the potassium salt of the anion-radical of tetraphenylethylene in THF does not exist, whereas the dipotassium salt of the dianion is stable because it is better solvated. Therefore immediately after its formation the anion-radical of tetraphenylethylene disproportionates by the route shown in Scheme 13 which demonstrates the formation of stable ionic pairs.[31]

The decomposition of ionic pairs hinders the disproportionation, and in HMPA the anion-radical of tetraphenylethylene acquires the ability to exist for a long time[31] (Scheme 14). This is essential when choosing solvents for the ion-radical polymerization.

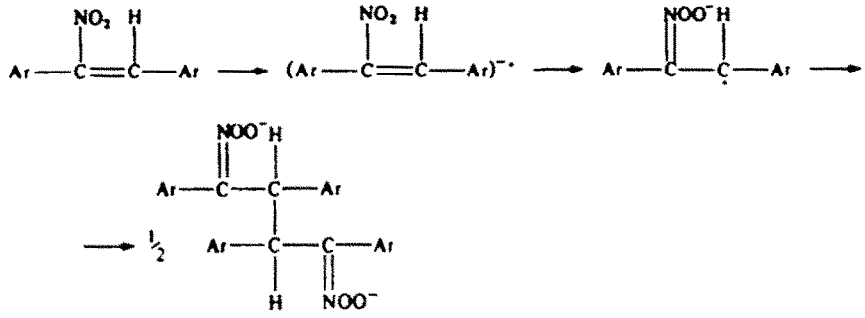
Another important direction of synthesis is the ion-radical dimerization. The investigation of α-nitroolefins dimerization under the action of the cyclooctatetraene dianion or at an electrode has demonstrated[32] that it proceeds not as the dimerization of two anion-radicals but rather as the interaction of the α-nitroolefin dianion with the neutral molecule. At first, however, the former direction

$$(Ph_2C{=}CPh_2)^{-\cdot}K^+ + HMPA \longrightarrow (Ph_2C{=}CPh_2)^{-\cdot}/HMPA/K^+$$

$$(Ph_2C{=}CPh_2)^{-\cdot}/HMPA/K^+ + (Ph_2C{=}CPh_2)^{-\cdot}/HMPA/K^+ \rightleftharpoons$$

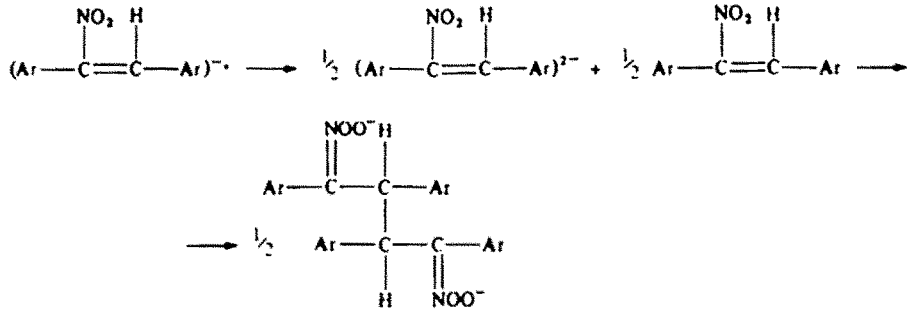
$$\rightleftharpoons Ph_2C{=}CPh_2 + (Ph_2C{=}CPh_2)^{2-}/HMPA/2K^+$$

Scheme 14.



Scheme 15.

seemed to be more probable (Scheme 15) because the nitro group converting into the nitronate group ($-NO_2 \rightarrow =NOO^-$) following electron transfer makes the carbon adjacent to the olefin bond radically nonsaturated. This dimerization, however, requires a high activation energy because it presupposes that two negatively charged particles are brought closer together and the bond forms between them. The dianion interacting with the neutral molecule requires less energy (Scheme 16).



Scheme 16.

The same holds true for cation-radicals. For example, two cation-radicals of 4-methoxybiphenyl dimerize in acetonitrile at an activation energy of not below 10 kcal/mol, whereas the interaction of the cation-radical with the neutral molecule requires no activation energy and the rate of the process is independent of temperature.[33]

6. *Orientation at substitution and distribution of spin density in the substrate ion-radical*

The ESR spectrum of ion-radicals gives the quantitative distribution of the spin density. The ESR spectrum determines the super-fine interaction (SFI) constant for the i^{th} hydrogen, a_i^H. The constant is directly proportional to the spin density at the i^{th} carbon carrying the i^{th} hydrogen.

Needless to say, a correlation between a_i^H and the direction of substitution does not indicate that the reaction necessarily takes the ion-radical pathway. In other words, the correlation may represent the relationship, say, between the orientation and the tendency of a substrate to locate a charge, or between the electronic structure of the transition state and the distribution of the spin density in the substrate ion-radical, etc. For example, the orientation at the electrophilic substitution of aromatic compounds (Table 1) correlates with a_i^H of the corresponding cation-radicals. When trying to establish such

Table 1. Properties of aromatic compounds and corresponding cation-radicals

Compound	Reaction	Reactivity	a_i^H
N,N-Dimethylaniline	Bromination	4 > 2 > 3[35]	4 > 2 > 3[36]
Naphthalene	Nitration	1 > 2[37]	1 > 2[38]
	Tritiation	1 > 2[39]	
Anthracene	Acylation	9 > 1 > 2[38]	9 > 1 > 2[38]
Biphenylene	Nitration	2 > 1[40]	2 > 1[41]
Triphenylene	Nitration	2 ≈ 1[42]	2 ≈ 1[29]
Azulene	Nitration	1 > other[43]	1 > other[44]

Table 2. Constants SFI and activation energy in the ethoxy group substitution for chlorine when treating nitro- and dinitrochlorobenzenes with a mixture of ethyl alcohol and piperidine

Compound	Constants SFI, G[48,49]	E_{act} (kcal/mol)[50]
1. Nitrobenzene	$a_2^H = a_6^H = 3.30$; $a_4^H = 3.82$	-
2. 2-Chloronitrobenzene	$a_6^H = 3.30$; $a_4^H = 3.92$	18.1
3. 4-Chloronitrobenzene	$a_2^H = a_6^H = 3.42$	17.1
4. 1,3-Dinitrobenzene	$a_2^H = 2.77$; $a_4^H = a_6^H = 4.49$	—
5. 1,3-Dinitro-2-chlorobenzene		12.2
6. 1,3-Dinitro-4-chlorobenzene		10.7

relationships, one should bear in mind that an unpaired electron localizes differently in ion-radicals of unlike signs.[34] The results of investigations[35-44] are summarized in Table 1. They demonstrate the symbiotic correlation between the distribution of spin density in cation-radicals and the direction of electrophilic substitution. In particular, azulene is nitrated most easily at position 1 which has the greatest spin density in the cation-radical (the anion-radical of azulene has the greatest spin density not at position 1 but at position 6).[46,47]

The orientation given in Table 1 is observed at the standard electrophilic substitution of neutral molecules. This is not exactly so, however, for triphenylene. The calculations by the Hückel MO method demonstrate[45] that in uncharged triphenylene the most reactive is position 2. In the cation-radical the most reactive is not only position 2 but also position 1.[28] As follows from Table 1, the experimental data on orientation at the triphenylene nitration agree with the results of calculations only when the intermediate particle is the cation-radical of triphenylene and not triphenylene itself.

Interesting data can also be cited on nucleophilic reactions. Relative rates of the chlorine substitution in nitrochlorobenzenes under the action of different nucleophilic reagents accord well with a_i^H of the anion-radicals. It is true, one is forced to rely on the values of a_i^H of the anion-radicals not carrying chlorine. The spin of the chlorine nucleus is 3/2 and that of proton is 1/2. As a result, splitting at chlorine is 1/10 of that at proton at the same spin density on the nucleus. In passing from nitrochlorobenzene to nitrobenzene, SFI constants of the corresponding anion-radicals practically do not change. As follows from Table 2, $a_2^H(a_6^H)$ of the 4-chloronitrobenzene anion-radical is close to $a_2^H(a_6^H)$ of the nitrobenzene anion-radical; the pair 2-chloronitrobenzene and nitrobenzene shows the same agreement between a_6^H and a_4^H. In the anion-radical of nitrobenzene $a_4^H > a_2^H$. The substitution of ethoxyl for chlorine in 4-chloronitrobenzene proceeds much easier and requires a lower activation energy than the same substitution in 2-chloronitrobenzene. The spin density in position 4 of the anion-radical of 1,3-dinitrobenzene is greater than in position 2 ($a_4^H > a_2^H$). Therefore 1,3-dinitro-4-chlorobenzene is more active in nucleophilic substitution than 1,3-dinitro-2-chlorobenzene.

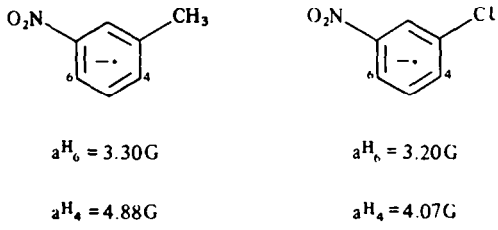
The methoxide ion[51] replaces chlorine in 4-chloro-3-methylnitrobenzene more rapidly than in 6-chloro-3-methylnitrobenzene (Table 3; nos. 1 and 2). This agrees well with the theory that the anion-radical of 3-methylnitrobenzene has a greater spin density in position 4 than in position 6[52] (compare with Scheme 17). The SFI constants of the 3-nitrochlorobenzene anion-radical[49] (Scheme 17) and relative rate constants of methoxy ion substitution[51] for chlorines at the i^{th} carbons (Table 3; nos. 3 and 4) correlate in the same way.

This argument in support of the ion-radical pathway has no value unless combined with other proofs. However, an analysis of the correlation between the orientation at substitution and the electronic structure of an ion-radical will help elucidate the problem in full.

Nucleophilic substitution reactions proceeding by the chain ion-radical mechanism also demonstrate a certain correlation between the distribution of electronic density in ion-radicals and the

Table 3. Relative rate constants of the methoxy ion substitution for chlorine (25°, MeOH)[51]

No.	Initial compound	Reaction product	k_{rel}
1.	6-Chloro-3-methylnitrobenzene	6-Methoxy-3-methylnitrobenzene	1
2.	4-Chloro-3-methylnitrobenzene	4-Methoxy-3-methylnitrobenzene	3.6
3.	3,6-Dichloronitrobenzene	3-Chloro-6-methoxynitrobenzene	1
4.	3,4-Dichloronitrobenzene	3-Chloro-4-methoxynitrobenzene	2.6

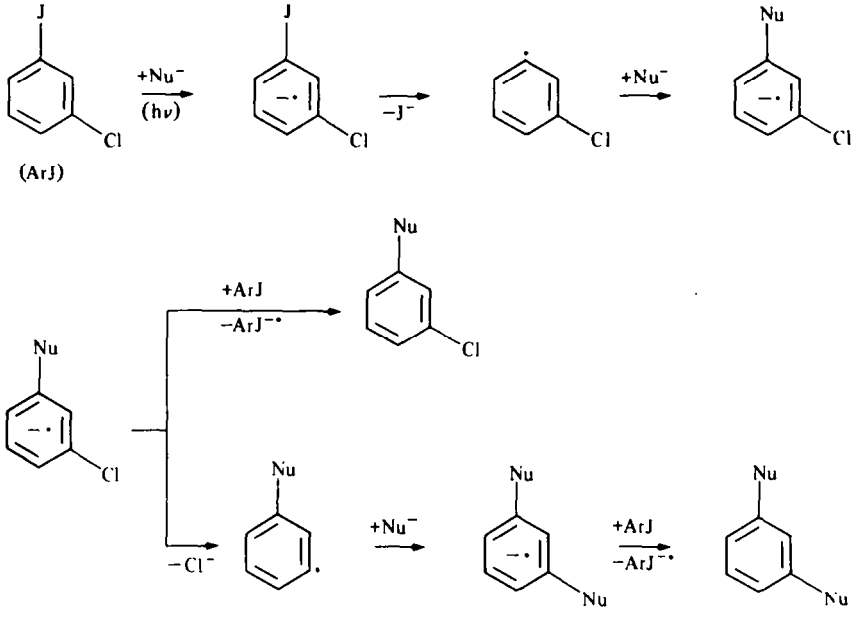


Scheme 17.

reactivity of the corresponding uncharged substrates. As has been reported,[53,54] *m*-chloroiodobenzene reacts (photoirradiation, liquid ammonia) with such nucleophiles as diethylphosphite and thiophenolate. Under similar reaction conditions monosubstitution yielding diethyl-*m*-chlorobenzene phosphonate prevails in the first case, whereas in the second the main product is *m*-(bisphenylthio)benzene. When the reaction involves the diethylphosphite ion, a certain degree of disubstitution can be achieved by lowering the concentration of the substrate. Thus, when the concentration of *m*-chloroiodobenzene is 0.1 M, the reaction produces only the product of monosubstitution, but when it is lowered to 0.008 M, disubstitution (up to 15%) proceeds concurrently with monosubstitution.

It has been revealed[53,55] that the products of the thiophenolate and diethylphosphite disubstitution do not form from monosubstituted derivatives. The monosubstituted product is 20 times less active than the initial substrate as regards thiophenolate. The $S_{RN}1$ model takes all these facts into consideration (Scheme 18).

The scheme shows that the course of the reaction is determined by the fate of the monosubstituted product in the anion-radical form. Because $(EtO)_2P(O)$ is a stronger acceptor than the PhS group, anion-radicals *m*-$ClC_6H_4SPh^{-\cdot}$ decompose much easier than anion-radicals *m*-$ClC_6H_4PO(OEt)_2^{-\cdot}$. A more stable anion-radical lives until the moment when it meets the initial substrate and gives it an electron, thus producing a monosubstituted derivative. By contrast, a less stable anion-radical cleaves the chloride ion before it is subjected to one-electron oxidation, and the process tends towards disubstitution. The frequency of collisions of the chlorine bearing anion-radical with the initial substrate is greater the higher the concentration of the substrate. Therefore diluting the solution promotes disubstitution. The ion-radical disubstitution also proceeds stepwise. What is quite important is that the second step involves the product in the anion-radical form, which is far more



Scheme 18.

reactive than the corresponding uncharged molecule. All these simple observations considered together support the $S_{RN}1$ mechanism of the reaction.

To conclude, it should be noted that it is necessary to check whether the $S_{RN}1$ mechanism is operative when passing from one reaction system to another, even if they are similar. Thus, ketene enolates easily substitute chlorine in position 2 of the electrophilic nucleus of pirazine (1,4-diazabenzene), and even in the dark the reaction proceeds by the $S_{RN}1$ mechanism.[56a] It might be expected that the introduction of the second chlorine in the *ortho* position to another nitrogen in the electrophilic nucleus of pirazine should better promote the ion-radical pathway. However, 2,6-dichloropirazine in the dark or subjected to light reacts with the same nucleophiles by the S_N2 and not by the $S_{RN}1$ mechanism.[56b] The authors[56b] are of the opinion that two halogens in the pirazine cycle facilitate the formation of the σ-complex to the extent that the dehalogenation of the anion-radicals in the solution and a subsequent nucleophilic attack of a free pirazine radical become almost impossible. Thus, the reaction may proceed by either of the mechanisms, that involving and that not involving the intermediate σ-complex, and only special identification experiments can tell which is the true one.

7. Physical methods of revealing ion-radicals

Previous sections treated the substances entering into the ion-radical conversions and analyzed the resulting products. However, in order to get a deeper insight into the course of the process it is necessary to reveal the intermediate particles participating in conversions. In other words, we must give direct proofs of the formation of ion-radicals. Moreover, it should be demonstrated that the ion-radicals form not on the parallel but on the main pathway of the reaction. And finally, it is essential to discover the particles generated in the ion-radical decomposition if the process, in general, has a radical nature.

Electron spin resonance. This method unambiguously establishes the presence of particles bearing unpaired electrons (ion-radicals and radicals). The ESR spectrum quantitatively characterizes the distribution of the electron density within the paramagnetic particle by a superfine ESR structure. This establishes the nature and electronic configuration of the particle.[57-60]

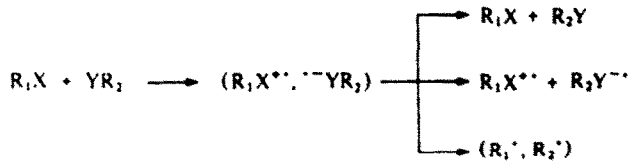
The ESR method provides information only on particles which exist for more than 1×10^{-3} s. In order to investigate short-lived radicals their concentration in the registration system of the ESR spectrometer should be stationary; this means that flow methods should be used. They allow one to study reactions with conversion times below 10^{-4} s.

Chemically induced dynamic nuclear polarization (CIDNP). CIDNP is several orders more sensitive than ESR as regards the detection of the ion-radical stages of reactions. Particles with uniformly populated Zeeman levels give normal NMR spectra. Molecules produced as a result of a radical–radical recombination may have nonuniformly populated Zeeman levels. This leads to the abnormal NMR behaviour called chemically induced dynamic nuclear polarization: enhanced absorption at a positive polarization and emission at a negative polarization. The CIDNP signals are observed immediately after the particle formation within the period of time necessary for nuclear relaxation. This time is 1–30 s. The NMR spectra often visualize the multiplet effect that is the lines in spin multiplet in high and low fields have opposite signs revealing both emission and absorption. The peculiarities of CIDNP, its theory and kinetics are thoroughly discussed.[61] The monograph gives numerous examples of CIDNP observed with oxidation–reduction reactions (interaction of alkyllithium with alkyl halides), reactions of diazonium and iodonium salts, reactions of organometallic compounds, oxidation and photochemical electron transfer.

The CIDNP method provides the following information.[61] It (i) proves that the reaction proceeds through intermediate paramagnetic particles (ion-radicals, radicals, biradicals); (ii) establishes which radical pair gave rise to a molecule and determines spin multiplicity of the reacting particles forming a radical pair; (iii) evaluates by the kinetics of nuclear polarization the rate constants of the ion-radical conversions and their activation energies.

The CIDNP method is not universal. It has certain drawbacks: the polarization is weak and is hardly detected in reactions involving extremely short-lived radicals and, if so, it disappears quickly. It is often difficult to attribute the polarization to the products of the main, rather than of the side or reverse conversions. The latter threat is most serious for the reactions with the participation of ion-radicals: the formation of end products often proceeds concurrently with the restoration of the initial neutral molecules owing to a reverse electron transfer (Scheme 19).

As follows from Scheme 19, not only the end products but also the initial molecules should be polarized. Besides, one of the components of the ion-radical pair may exchange electrons with the



Scheme 19.

neutral starting molecule, for example

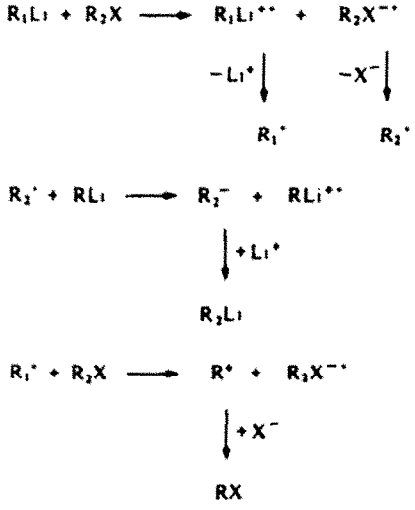
$$RXY^{\cdot -} + RXY \rightarrow RXY + RXY^{\cdot -}.$$

This exchange reduces the residence time of ion-radical $RXY^{\cdot -}$ in the pair and lowers the net polarization. This and some other phenomena which can be attributed to electron exchange led to a loss of memory of nuclear-spin states. And finally, the initial polarization may be "scattered" as a result of a chain ion-radical process. This is illustrated in Scheme 20.[62]

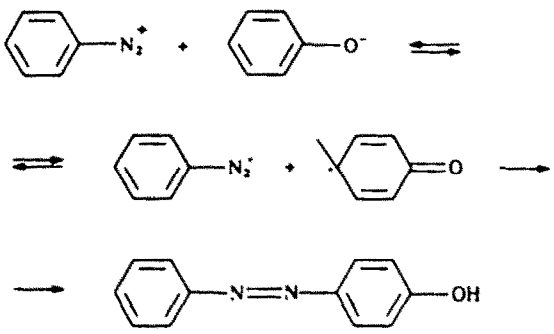
Buchachenko[61] advances another theory. He bases his reasoning on the absence of the CIDNP signals for the reaction of n-butyl iodide with tert-butyllithium conducted in ether at $-70°$. The halogen and metal quickly exchange under these conditions, but the C—C bond does not form. In contrast to Scheme 20, the theory[61] assumes that the radicals produced following electron transfer form complexes with the alkyllithium associates. Alkyllithium forms stable hexamers (two pyramids having a common base) and tetramers (tetrahedrons). These associates exist even in the gas phase and are revealed by mass spectroscopy. A radical bonded in such a cluster produces a paramagnetic widening of the NMR signals. This makes them nonobservable long before the end of the reaction. So, in this case, we should speak not about the absence of the CIDNP effect but about its masking.

Another word of caution may be in order. The spectra may visualize nuclear polarization of products due to polarization of initial substances. Bubnov and co-workers[63] recorded ^{15}N-NMR spectra to investigate the azocoupling of benzyldiazonium tetrafluoroborate with sodium phenolate in methanol. Benzyl diazonium was prepared from aniline-^{15}N and $H^{15}NO_2$. The spectrum demonstrated a strong polarization of signals from the azo dye immediately following mixing of solutions of the diazo compound and phenol. The signal from the initial diazonium salt was also polarized. The researchers[63] drew the conclusion that the azo dye is produced according to Scheme 21; the nuclear polarization of the diazonium nitrogen was regarded as evidence of the reversibility of the electron transfer stage.

The following treatment of the CIDNP results arouse serious objections.[64,65] Lippmaa *et al.*,[64] investigating the same reaction, revealed a strong ^{15}N, ^{13}C and ^{1}H CIDNP effect. They state that ^{13}C nuclei in the phenoxyl ring of the azo dye are not polarized, whereas the polarization of ^{15}N nuclei of the



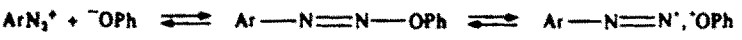
Scheme 20.



Scheme 21.

azo bond and ^{13}C nuclei at positions 1 and 2 of the phenyl ring is an exact replica of the polarization of the same nuclei in the diazonium salt. This has led to the conclusion that the diazo component polarizes as a result of the side reactions and that it is the diazo component that brings it to the azo dye.[66] Thus, the CIDNP effect does not support the mechanism presented in Scheme 21.

Several explanations of the observed CIDNP effect have been proposed. We want to discuss here one of them because it seems to explain a whole range of interactions of diazonium salts with oxyanions, the interaction which is accompanied by a pronounced polarization of nuclei. The reaction of diazocation with phenolate yielding the azo dye may proceed through the formation of the diazoether. Kekulé[67] came to this conclusion in 1870. Zollinger, considering this conclusion, proposed and explained the mechanism by which the diazo ethers convert into the C-diazo compounds, that is into the oxyazo dyes.[68] The diazo ether preliminarily dissociates into the phenolate ion and the diazonium ion, in other words two-stage intermolecular reaction takes place. The CIDNP effect suggests that the diazo ether may reversibly convert into the radical pair (Scheme 22).



Scheme 22.

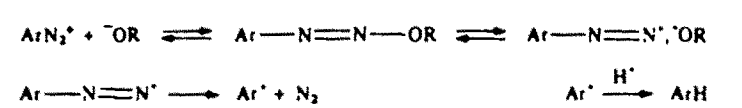
While interacting with the alkoxyl anions, the diazonium cation also produces a primary diazo ether although it can give no azo dye. ^{15}N and ^{13}C nuclei of aryldiazonium borofluoride enriched with ^{15}N in both positions become polarized in the presence of sodium alcoholates.[69] The reaction yields benzene showing nuclear polarization.[70] The data on kinetics and the CIDNP results[71,72] agree well with Scheme 23 which has much in common with Scheme 22.

As follows from the above, the CIDNP method is of great help to the chemist. In the present state of the art, however, it cannot always give straightforward information, first, because the CIDNP effect may be masked and, second, because errors may creep into its interpretation.

Other physical methods. Magnetic susceptibility of paramagnetic particles in solutions[73] is used to determine the concentration of ion-radicals but yields no structural information. Instruments for such measurements are only rarely used in chemical laboratories. Besides, special devices should be elaborated to conduct investigations at different temperatures.

The NMR method determines the concentration of ion-radicals and sometimes establishes their structure. The concentration of ion-radicals in solutions may be determined either directly by the intensity of the ion-radical signals, or indirectly by splitting of the standard signal[74a] or by a chemical shift of the solvent signal[74b] observed in the presence of the ion-radical.

Spectrophotometry. Stable ion-radicals have, as a rule, a deeper colouring than the initial neutral molecules. An unpaired electron on the molecular orbital increases the molecule polarizability and facilitates its excitation by light. This enhances the intensity of absorption and shifts it to the region of



Scheme 23.

higher wavelengths. Therefore, ion-radicals can be quite easily revealed by electronic spectroscopy. This method is often applied to investigate the kinetics of the ion-radical reactions and to establish the significance of the ion-radical pathway. For example, the ESR method has revealed that the methoxylation of *p*-nitrochlorobenzene produces ion-radicals of the initial substance. It has also shown that besides the main product, *p*-nitroanisole, the reaction yields the side product, *p*-nitrophenol (up to 15%).[75] The kinetics of consumption of the *p*-nitrochlorobenzene anion-radicals was studied spectrophotometrically.[76] The investigation has demonstrated that *p*-nitrophenol is produced from the anion-radicals of the initial *p*-nitrochlorobenzene and that almost all anion-radicals convert into nitrophenol. Solodovnikov[76] came to the conclusion that the anion-radicals of *p*-nitrochlorobenzene are produced by the reaction parallel to substitution. Then, it should be assumed that the reaction proceeds either by a nonradical mechanism or by a "hidden-radical" mechanism which implies that particles of a radical nature are produced and unite in a solvent cage without passing into a solvent pool. This conclusion caused objections.[77] The author[77] points out that the kinetic result[76] may also be obtained in the case of a sequential reaction yielding anion-radicals of *p*-nitrochlorobenzene and then of *p*-nitroanisole, when one of these stages is the limiting stage, say, formation of the anion-radical of the initial substrate upon its interaction with the methylate anion. Abe and Ikegame[23] investigating the kinetics of reaction between *p*-dinitrobenzene and alkali, demonstrate that the formation of anion-radical is the limiting stage. The author[77] considers the assumption that all the anion-radicals of *p*-nitrochlorobenzene convert into *p*-nitrophenolate invalid because these anion-radicals may be consumed in other reactions. If the presence of oxygen leads only to *p*-nitrophenolate (the side product), then it would hardly promote the nucleophilic substitution of methoxyl for chlorine.[77] The discussion of errors which could be introduced[76] is of a special methodological interest. Shein[77] pays attention to the following facts. Kinetic calculations usually take the highest molar extinction of *p*-nitrophenolate increased almost twenty times. This is clearly seen when comparing values taken by Shein[77] and Abe.[23] Dimethylsulphoxide used as a solvent[76] may contain water and CH_3SNa. Water may hydrolyze the initial *p*-nitrochlorobenzene (spectrophotometry uses solutions extremely diluted with respect to the substrate). CH_3SNa may lead to *p*-nitrophenylmethyl sulphide and its anion-radical, and this was not taken account of in the kinetic equations. Solodovnikov[76] considers neither the production of the anion-radical of *p*-nitroanisole nor the formation of the other products of a deeper reduction of the substrate.

When the kinetics of ion-radical reactions is investigated spectrophotometrically, solvents should be analyzed for purity, reagents and products should be checked against the material balance. These requirements are not simple but they are essential in order to obtain adequate kinetic data.

IR spectroscopy. When conducted in solvents not masking the bands of the ion-radical particles and when the particles themselves are stable, the IR spectroscopy may be used to advantage to identify their structure (by a change in the number of ion-radical absorption bands or by a different pattern of their distribution as compared with the initial neutral molecule) and perform quantitative determinations (by the intensity of bands). Moreover, it determines the localization of spin density, i.e. answers the key question concerning the structure of ion-radicals. IR investigations of the metalloporphyrine cation-radicals have established that spin density and a positive charge are localized not on the iron but rather on the porphyrin ligand.[78]

Electrochemical modelling of ion-radical reactions. Kitaev *et al.*[79] discuss this method in detail. Whether the data of electrode reactions may be carried over to the ion-radical conversions or not, is decided in every particular case. Electron transfer in the homogeneous medium and at the electrode have much in common, but still the differences are great.[80]

Mass spectrometry. The behaviour of ion-radicals in the mass spectrometer chamber opens up principal venues of their alteration. The liquid-phase chemical reaction, however, cannot always provide such possibilities. This is quite evident and needs no comment.

8. *Chemical probing of ion-radical reactions*

Initiation of polymerization of vinyl compounds. It is not always an easy matter to establish the ion-radical mechanism of reactions even with the help of modern physical methods. This is especially so for the reactions producing unstable phenylthiyl radicals from the thiophenolate ion. This radical, however, can be trapped by introducing styrene into the system. Even minute quantities of the phenylthiyl radical cause styrene polymerization. Thus, the reaction of sodium thiophenolate with alkyl halides or 2-butylnosylate,[81] or with benzyl halides[82] proceeds through a stage of electron

$$PhSNa + AlkHal \longrightarrow PhS^{\cdot} + (AlkHal)^{-\cdot}Na^{+} \longrightarrow NaHal + PhSAlk$$

Scheme 24.

transfer producing the phenylthiyl radical. As a result styrene polymerizes with the insertion of the phenylthiyl radical. The sulphur-containing oligomer was separated and characterized. The oligomer does not form when thiophenolate is mixed with styrene in the absence of the acceptor component (alkyl halide or nosylate). The introduction of the radical trap—phenylterbutylnitrone—decelerates the reaction of the acceptor component with thiophenolate, and ESR spectroscopy registers the product of the phenylthiyl radical addition to nitrone. This indicates that the phenylthiyl radicals form on the main pathway of the reaction (Scheme 24).

The presence of the phenyl radicals in the substitution of the nitro for the diazonium group in the reaction of benzol diazonium salts with sodium nitrite has been demonstrated in the same way as for reaction 24. Acrylonitrile introduced into the reaction mixture polymerizes; the polymerization takes place in nitrogen and oxygen inhibits it.[83a] This supports the scheme of reaction analogous to Scheme 11. However, the initiation alone of polymerization of vinyl compounds (indicators) cannot be regarded as sufficient proof of the ion-radical pathway of reactions. Singh *et al.*[83a] report that benzene- and *p*-nitrobenzenediazonium fluoroborates convert into nitro- and *p*-dinitrobenzenes under the action of sodium nitrite in methanol, whereas *p*-methoxybenzene diazonium does not produce nitroanisole. The fact that *p*-methoxybenzene diazonium falls out of the series is easily explained: the *p*-methoxyphenyl radical is incapable of coupling with the nitrite ion, and the sequence of stages illustrated in Scheme 11 becomes impossible.[83a]

Thus, the separation of polymers from the reaction mixture containing the vinyl compound additive indicates that the substrate produces a radical at the intermediate stage. The latter adds to a "probe" and forms a radical adduct with the vinyl monomer, and initiates the monomer polymerization. Sometimes, however, the radical adduct may add not to the "probe"-monomer but to the main reagent. The polymerization does not start but the reaction yields a low-molecular individual substance containing fragments of substrate, monomer and reagent. To illustrate, we shall consider the reaction of perfluoroalkyl iodide (substrate) with the nitropropenide salt (reagent) in the presence of the monomeric probe (vinyl acetate, methylmetacrylate, styrene).[83b] Electron transfer from the reagent to the substrate is accompanied by cleavage of the iodide ion and formation of the perfluoroalkyl radical. The latter attacks the monomer in the reaction sphere. The radical adduct in the case of the above listed vinyl monomers adds to the nitropropenide ion at a greater rate than to another molecule of the monomer.

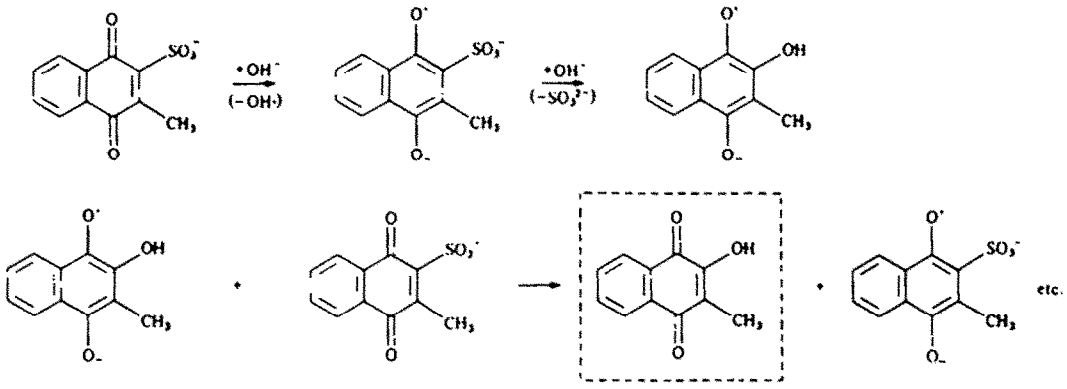
Method of inhibitors. Each ion-radical reaction involves electron transfer and further conversion of ion-radicals. Ion-radicals may either be consumed within the solvent cage or pass into the solvent pool. If they pass into the solvent volume, the method of inhibitors may determine whether the ion-radicals were produced on the main pathway of the reaction, in other words, whether they were spent to obtain the desired product. The inhibitor is such that it is able to oxidize the anion-radical or reduce the cation-radical; the yield and the rate of formation of the end product are carefully watched over. It is quite evident that both anion- and cation-radicals produced upon electron exchange between the substrate and reagent can not always leave the cage and exist in solution for a long time. The nucleophilic substitution of chloride in 2,4-dinitrochlorobenzene (substrate) by the diethylamino group from triethylamine furnishes a good example of this. The anion-radical of the substrate and the cation-radical of the reagent pass into the solvent volume.[84a] Therefore, acceptor compounds (*p*-benzoquinone, tetracyanoethylene, tetracyanoquinodimethane) and electron donors (potassium iodide, iron(II) sulphate, tetramethylparaphenylenediamine) inhibit the substitution.[84a]

Sometimes the substrate anion-radical quickly decomposes producing the organic radical and only then converts it into the final product. In this case use can be made of usual inhibitors of radical reactions and the reaction mechanism can be disclosed by a nature of products. Thus, transfer of electron from the anion-radical of naphthalene to organomercury halides gives naphthalene and the substrate anion-radical. The latter decomposes in two stages:

$$(RHgHal)^{-\cdot} \xrightarrow[-Hal^{-}]{} RHg^{\cdot} \xrightarrow[Hg^{0}]{} R^{\cdot}.$$

Then, symmetrization proceeds by the following scheme:

$$R^{\cdot} + R\text{-}HgHal \rightarrow (R_2HgHal)^{\cdot} \xrightarrow{+e} (R_2HgHal)^{-} \xrightarrow[-Hal^{-}]{} R_2Hg.$$



Scheme 25.

Cumene (H· donor) inhibits the symmetrization. The main direction becomes the reducive demercuration because radicals R· controlling the process leave the sphere of the reaction:[84b]

$$R^{\cdot} + H^{\cdot} \rightarrow RH.$$

Widely encountered are the reactions which produce unstable radicals of the type ·OH, ·OAlk from reagents $^{-}$OH, $^{-}$OAlk and rather stable anion-radicals from substrates, say, quinones.

Sodium methylate acting on 2-chloroanthraquinone substitutes the methoxy group for chlorine and produces anion-radicals of the substrate.[84c] The study of kinetics has demonstrated that the amount of the substrate anion-radicals first increases and then sharply decreases. The inhibitor (*p*-benzoquinone) decelerates the formation of the anion-radicals. The rate of formation of 2-methoxyanthraquinone also decreases.[84c] If the anion-radicals were produced on the side pathway, the rate of formation of the end product upon the introduction of the inhibitor should not have decreased. Moreover, it should even rise because the oxidation of the anion-radicals regenerates the uncharged molecules of the substrate. Thus, the anion-radical mechanism controls this reaction.

As has been reported, other nucleophilic reactions in the anthraquinone series also involve the production of anion-radicals. These reactions are: the hydroxylation of 9,10-anthraquinone-2-sulphonic acid;[85,86] the hydroxylation, alkoxylation and cyanidation in the homoaromatic ring of 9,10-anthraquinone condensed with the 2,1,5-oxadiasole ring at positions 1 and 2.[87] The researchers[85-87] are of the opinion that one-electron reduction of quinone proceeds in parallel to the main nucleophilic reaction. The concentration of the 2-anthraquinone-2-sulphonate anion-radicals, for example, becomes independent of the duration time of reaction with alkali, and the total yield of the anion-radicals does not exceed 10%.[85,86] Inhibitors (oxygen, potassium ferricyanide) prevent the formation of the anion-radicals, and the yield of 2-oxyanthraquinone even somewhat increases.[85,86] In this case, the anion-radical pathway is not the main one. Only when it is strongly supported in each specific instance, may the anion-radical stage be included in the mechanism of reaction. It is of interest that another representative of quinones—sodium 3-methyl-1,4-naphthoquinone-2-sulphonate—substitutes hydroxyl for the sulpho group mainly by the ion-radical mechanism. The initial stage involves the formation of the substrate anion-radicals, and the end product is 2-oxy-3-methyl-1,4-naphthoquinone. As the reaction proceeds, the quantity of the anion-radicals reaches a maximum, and then immediately drops. At this moment the concentration of the end product starts to rise.[88] Upon the introduction of inhibitors (oxygen, potassium ferricyanide) neither the anion-radicals accumulate, nor the end product forms.[88] This indicates that the hydroxylation of 3-methyl-1,4-naphthoquinone-2-sulphonic acid proceeds at the expense of the ion-radicals by the chain mechanism (Scheme 25).

The method of inhibitors has demonstrated that the substitution of chlorine in triphenylchloromethane by the tert-butyl anion does not follow the mechanism of one-electron transfer. So far, the researchers[89,90] have thought that the reaction occurs by Scheme 26.

The scheme postulated the formation of radical pairs following the interaction of two particles without free valences. When the solution of triphenylmethyl chloride in THF was mixed with potassium t-butylate in the radiospectrometer resonator, the ESR spectrum visualized the presence of the triphenylmethyl radical. The intensity of this signal first increases reaching a maximum and then

$$Ph_3CCl + t\text{-}BuOK \longrightarrow (Ph_3CCl)^{-\cdot} + (t\text{-}BuOK)^{+\cdot} \longrightarrow$$

$$\longrightarrow KCl + Ph_3C^{\cdot} + t\text{-}BuO^{\cdot}$$

$$Ph_3C^{\cdot} + t\text{-}BuO^{\cdot} \longrightarrow Ph_3COBu\text{-}t$$

$$2Ph_3C^{\cdot} \longrightarrow \text{Dimer}$$

Scheme 26.

decreases to an equilibrium value. In the opinion of the authors,[89] the super-equilibrium concentration of the radicals agrees well with their generation at the primary stage of Scheme 26. In other words, the substitution product forms at the expense of the primarily generated radicals. The ESR spectrum fixes those triphenylmethyl radicals which failed to recombine with t-butoxyl radicals prior to their passage into the solvent pool.

The authors of a later work[91] suggest the mechanism given in Scheme 27.

m-Dinitrobenzene was added to a boiling solution of triphenylchloromethane and potassium tertbutylate in 2,2-dimethoxypropane.[91] In contrast to experiments conducted without the inhibitor, the yield of the substitution product markedly increased and the yield of the dimer decreased. Therefore the authors[91] conclude that the main pathway of the reaction does not involve the formation of the anion-radicals and radicals by Scheme 26. Scheme 27 suggests an alternative pathway, which is confirmed by a thorough structural analysis of the secondary products formed along with the t-butyl ester of triphenylcarbinole.[91-93]

Method of radical and spin traps. The method may be applied to the investigation of ion-radical reactions producing free radicals. They, as a rule, are not stable, and special traps—radical and spin—are used to reveal them.

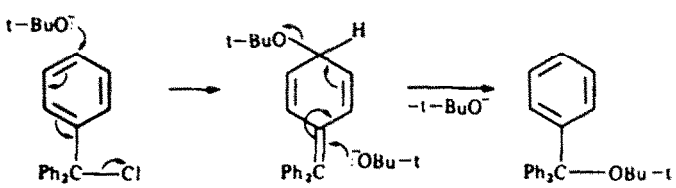
Radical traps belong to the class of stable free radicals, e.g. of the nitroxyl[94] or phenoxyl[95] type. Interacting with radicals produced by the reaction, radical traps give diamagnetic compounds. One can follow the progress of the reaction by a decreasing intensity of the ESR spectrum of the radical trap.

Nitroso compounds, nitrones and other diamagnetic molecules can be used as spin traps. Capturing radicals produced in the reaction, spin traps form so-called spin-adducts—stable nitroxyl radicals easily detectable by ESR spectroscopy. In other words, the progress of the reaction can be easily followed by an increasing intensity of the spin-adduct signal. The method of traps reveals radicals by the disappearance (or appearance) of the ESR signal.

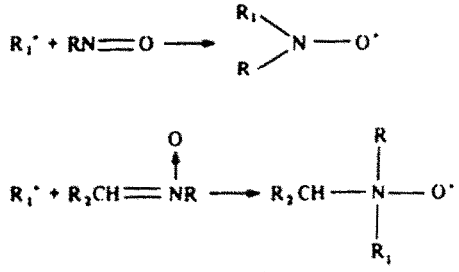
Radical and spin traps may inhibit the observed conversions, and this is their common drawback. Chain reaction may be inhibited either at the stage of generation or at the stage of branching. That part of a radical which combines with a trap leaves the sphere of reaction. Even small amounts of a trap can affect the kinetics of reaction if it proceeds by a chain mechanism. Traps can exchange electrons with the initial anion-radical or with the anion-radical of the product. As a result, spin traps convert to anion-radicals which distort the spectral picture. Radical traps capturing an electron produce diamagnetic compounds prior to combining with radicals. Therefore ESR spectra cannot be observed in this case. Even when a radical trap has an additionally strong electrochemically active group, a biradical is not formed, and so no ESR signal can be generated. Thus, piperidonenitroxyl in the presence of a donor undergoes one-electron reduction at the site of a free valence without the participation of the carbonyl group.[96]

Radical traps. The kinetics of a decrease of the ESR signal intensity represents the kinetics of the radical generation in the reaction mixture, because the adduct forms rapidly at a rate of diffusion.

Spin traps. The nitroxyl radicals produced from these traps by Scheme 28 give ESR spectra markedly differing in nitrogen splitting.[97,98] The splitting constant, a^N, depends on the nature of groups



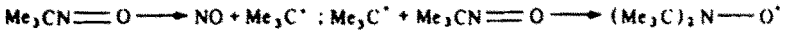
Scheme 27.



Scheme 28.

bonded to nitrogen. Splitting constants for the nitroxyl radicals vary over a wide range from 4–5 G for diacylonitroxyls[99] to 25–28 G for alkoxynitroxyls.[100] Thus, splitting constants of spin adducts are, in themselves, enough to give information on the nature of a short-lived radical fixed by a trap.

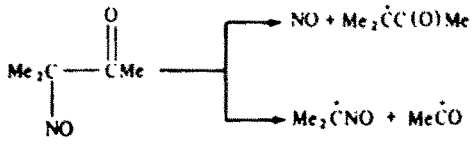
Types of spin traps. The most universal and therefore most commonly used trap is 2-methyl-2-nitrosopropane. The majority of radicals combining with it produce stable well identifiable spin-adducts.[101] When exposed to irradiation or at prolonged heating, the trap decomposes by Scheme 29. This should be borne in mind when studying the ion-radical reactions which involve thermal or light effect.



Scheme 29.

As follows from the scheme, the t-butyl radical adds to the initial molecule producing the nitroxyl radical. A triplet with a^N = 15–17 G, depending on the solvent,[102] corresponds to the radical. The triplet is often so intense that it can lap over lines corresponding to other spin-adducts.

2-Methyl-2-nitrosobutanone-2 exists in a non-active form of a dimer which dissociates in a solution to produce a monomer. UV-Irradiation or heating promote the dissociation causing at the same time the decomposition of the monomer into radicals according to Scheme 30.[103-105]

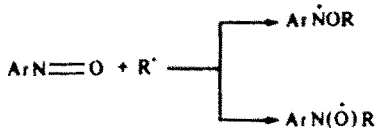


Scheme 30.

These radicals add to the initial molecule of a trap to produce spin-adducts. The nitrogen splitting constants of the latter spin adduct signals lie in the regions of 14–15 G and 7–8 G.

C-Phenyl-N-t-butylnitrone is rather stable; the formation of its spin-adducts is illustrated in Scheme 28. In these spin-adducts, and this is an essential feature, the unpaired electron interacts not only with the nitrogen nucleus but also with the nucleus of the hydrogen of the CH group neighbouring the nitrogen (Scheme 28).[106] This extends the identification possibilities of nitrone as a spin trap.

Nitrosobenzenes are commonly used as spin traps. They are stable and are used to advantage to identify radicals. Most often, however, not nitrosobenzene itself but its 2,4,6-trimethyl and tritert-butyl derivatives are utilized for the purpose; sometimes 2,3-dichloro- and 2,6-dichloronitrosobenzenes may be used. Nitrosobenzenes have a wider application than other traps. This is explained by the fact that the structure of spin-adducts strongly depends on the nature of the addable radical (Scheme 31). Spin-adducts differ in g-factor.[107,108] The primary alkyl, aryl and arylthio radicals form spin-adducts with a



Scheme 31.

$$RH + ArN{=}O \longrightarrow R^{\cdot} + ArN(\dot{O})H$$

$$R^{\cdot} + ArN{=}O \longrightarrow ArN(\dot{O})R$$

Scheme 32.

free valency at nitrogen, the tertiary radicals produce spin-adducts with a valency at carbon, and secondary radicals give both types of adducts.

The application of nitrosobenzenes has a number of peculiarities. First, nitrosobenzene may add a nucleophilic reagent (Nu^-). The product of addition easily oxidizes to generate radical $C_6H_5N(Nu)O^{\cdot}$. This predetermines the error in assigning the reaction to the ion-radical type. To avoid this, Lagercrantz[105] suggested the use of derivatives wherein the nitrogen of the nitroso group is sterically hidden. In these spin traps only oxygen of the nitroso group can react and only when attacked by radicals. Second, nitrosobenzenes may give spin-adducts interacting with solvents without the participation of reagents or substrate. Compounds of the nitrosobenzene series in n-decane, diphenylmethane, *o*-xylene, isopropylbenzene and ethylbenzene react as shown in Scheme 32.[109]

The reaction proceeds at room temperature or at moderate heating up to 60° without irradiation and in the absence of oxygen. The C—N bond in the nitroso compounds does not undergo thermal cleavage; any chemical initiation of the radical process is excluded.

The use of spin traps for quantitative measurements. ESR spectroscopy is a valuable tool when the need arises only to reveal and qualitatively characterize radicals. The question is whether the possibilities of this method can be extended as applied to radicals to conduct quantitative correlations by signal intensities. The quantitative estimates require primarily the knowledge of relative rates of radical addition to spin traps. Radicals, in general, can react with a trap and with medium M (Scheme 33).

Scheme 33 has been analyzed kinetically.[98,110] For spin-adducts to be produced in a sufficient concentration, $k_2 \gg k_{-2}$ and $k_3 \gg k_{-3}$. Then, the ratio of concentrations of nitroxyl radicals $R_1RNO^{\cdot}$ and $R_2RNO^{\cdot}$ in the solution under stationary conditions depends on k_1 and k_2 and also on the concentrations of trap and compound M. Thus, we get

$$\frac{(d[R_1RNO^{\cdot}]/dt)_{t\to 0}}{(d[R_2RNO^{\cdot}]/dt)_{t\to 0}} = \frac{[RNO^{\cdot}]}{[M]}.$$

The equation assumes that all radicals produced in the reaction are captured by a trap. At the early stages of the process the rate of addition may be compared only with the rate of radical recombination ($k_r = 10^8$–10^9 l mol^{-1} s^{-1}).[111] Therefore,

$$k_{add}[RNO^{\cdot}]([R_1^{\cdot}]+[R_2^{\cdot}]) \gg 10^8\text{–}10^9([R_1^{\cdot}]+[R_2^{\cdot}])^2,$$

where k_{add} is the addition constant. Because the concentration of $RNO^{\cdot}$ is equal to unity in the limit $k_{add} \gg 10^8$–$10^9([R_1^{\cdot}]+[R_2^{\cdot}])$. The concentrations of short-lived radicals $R_1^{\cdot}$ and $R_2^{\cdot}$ usually do not exceed 10^{-6}–10^{-7} M, and so $k_{add} \gg 10^2$ l mol^{-1} s^{-1}.

To conclude, the method of spin traps can be used to advantage for quantitative measurements in many radical reactions. The method can be applied when the rate constant of radical initiation is 10^7–10^8 l mol^{-1} s^{-1} and the trap concentration in the solution is not below 10^{-2} M.

The participation of traps in redox reactions. The problem has two aspects: the consumption of spin traps in one-electron oxidation (reduction) (1) of a free radical and (2) of an initial ion-radical.

Electron exchange between a trap and a free radical. A trap and an unstable radical may, in general, undergo the following reactions: addition producing an adduct, and electron transfer yielding a pair

$$R_1^{\cdot} + M \xrightarrow{k_1} R_2^{\cdot}$$

$$R_1^{\cdot} + RNO \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} R_1RNO^{\cdot}$$

$$R_2^{\cdot} + RNO \underset{k_{-3}}{\overset{k_3}{\rightleftharpoons}} R_2RNO^{\cdot}$$

Scheme 33.

$$Het{-}X + Nu^- \longrightarrow (Het{-}X)^{-\cdot} + Nu^\cdot$$

$$(Het{-}X)^{-\cdot} + (R)_2NO \longrightarrow Het{-}X + (R)_2NO^{-\cdot}$$

$$(Het{-}X)^{-\cdot} \longrightarrow Het^\cdot + X^-$$

$$Het^\cdot + Nu^- \longrightarrow (Het{-}Nu)^{-\cdot}$$

$$(Het{-}Nu)^{-\cdot} + (R)_2NO \longrightarrow Het{-}Nu + (R)_2NO^{-\cdot}$$

Scheme 34.

(cation from radical and anion-radical from a trap) or (anion from radical and cation-radical from a trap). And indeed, these reactions take place under certain conditions. Some radicals either do not form adducts with traps or their yield is very low.[112] So, the method fails to give information in cases where it should be effective. Sosonkin *et al.*[112] failed to reveal radicals RĊHOH with PhNO. This becomes clear when comparing the rate constants of the corresponding processes:[112] the rate constant of the radical addition to the trap, k_{add}, is 10^3–10^8 l mol^{-1} s^{-1} and that of electron transfer from RCHOH to PhNO, k_{tr}, is 10^9–10^{10} l mol^{-1} s^{-1}. It is readily apparent that the addition of the radical cannot compete with one-electron transfer. The authors[112] compared the redox potentials of a number of free radicals and spin traps; they demonstrated that the nitroso compounds can capture quantitatively only radicals having oxidation potentials below −0.6 V. Those are the alkyl, phenyl, RO˙, ȮH, ĊH$_2$COOH, ĊH$_2$COR and some other radicals. Nitrones, however, reduce at extremely negative potentials and cannot attract electrons from the strongest reducers—ketyl anion-radicals RRCO$^{-\cdot}$. Therefore nitrones can be widely used for quantitative capturing of radicals even if the latter are liable to one-electron oxidation.

So far, we have considered the acceptor properties of spin traps. Their donor properties are also known, although they are studied to a lesser extent. The literature data are scarce and cannot be generalized. Therefore, only some examples of one-electron oxidation of traps can be cited. Nitrosodurole forms stable cation-radicals upon photolysis in the presence of Ce^{4+} and U^{6+} in CF_3COOH.[113] Murabayashi *et al.*[114] observed the formation of cation-radicals from 2,4,6-tri(tert-butyl)nitrosobenzene subjected to the action of the 3-methylpentane molecular cation.

Thus, while investigating the mechanism of electron exchange, one should take into account the oxidation properties of a trap as to radicals or other electron donors present in the system. Because spin traps may be electron donors themselves, their oxidation potentials should be more positive than the oxidation potentials of reagents.

Electron exchange between a trap and the initial ion-radical. Previous paragraphs discussed the ability of spin traps to act as one-electron oxidizers. This property is even more pronounced in their reactions with anion radicals. Traps can block the ion-radical pathway; in other words, they inhibit the reaction. This may be explained by both oxidation of the substrate anion-radical and chain termination due to oxidation of the product anion-radical. An instructive example gives the inhibition of $S_{RN}1$ nucleophilic substitution of 2-chloroquinoxaline (Het-X) by the radical trap, di(t-butyl)nitrone, $(R)_2NO$ (Scheme 34).[115]

As is clear from what has been said above, no trap may turn out to be sufficiently effective. Davies and Robert[116] have established that oxygen reacts with diborane by a chain mechanism only when using galvinoxyl as an inhibitor.[116]

9. *Identification of some ion-radical reactions*

Interaction of hydroperoxides with phosphites and sulphides. It is well known that phosphites or sulphides added to stabilizers of polymeric materials considerably enhance their action. The additive decomposes hydroperoxides which decrease the stability of materials. Hydroperoxides decompose according to Scheme 35. While investigating the mechanism of the reaction, the authors[117] came to the conclusion that it has the ion-radical nature and proceeds by Scheme 36.

$$(R_1O)_3P + ROOH \longrightarrow (R_1O)_3P{=}O + ROH$$

$$R_1R_2S + ROOH \longrightarrow R_1R_2S{=}O + ROH$$

Scheme 35.

$$R'ElM + ROOH \longrightarrow (R'ElM^{+\cdot}, ROOH^{-\cdot})$$

$$R'ElM^{+\cdot}(OH), {}^{-\cdot}OR \longrightarrow \begin{cases} ROH + O{=}ElmR' \\ RO^{\cdot} + ElM^{+\cdot}(OH)R' \end{cases}$$

$$R'ElM = (R_1O)_3P, R_1R_2S$$

Scheme 36.

Scheme 36 presupposes a primary electron transfer from phosphite or sulphide to hydroperoxide. This yields the ion-radical complex which monomolecularly converts into the radical pair in the solvent (benzene) cage. The pair disappears either upon the disproportionation of radicals in the cage or upon the dissociation.

The ESR method reveals the cation-radicals of donors in cases when the donors contain the stabilizing groups 4,4'-dimethoxyphenyl sulphide or pyracatechine-tri(t-butyl)phenyl phosphite. Radical trap 2,2,6,6-tetramethylpiperidine-1-oxyl ($NO^{\cdot}$) reacts under the conditions of experiment (benzene, 20°) neither with hydroperoxides nor with phosphites or sulphides taken separately. However, when they are introduced into the reaction mixture together, $NO^{\cdot}$ starts to decay. The rate of the $NO^{\cdot}$ decay was determined by ESR spectroscopic methods, while the rate of the ROOH consumption in the reaction with RElm was discovered through polarography (by evaluating the residual part of ROOH). The rate constants of both processes proved to be practically the same. This means that $NO^{\cdot}$ decays only at the expense of the main process (Scheme 36), and the kinetics of decay fully corresponds to that of the bimolecular reaction (Scheme 35). The rate of the $NO^{\cdot}$ consumption is almost independent of its concentration in solution. The radicals formed from the radical pair are extremely active. In the presence of oxygen, however, the rate of the $NO^{\cdot}$ consumption markedly decreases (when $[O_2]_0 \gg [NO^{\cdot}]_0$). This is explained by the fact that oxygen converts a considerable part of active radicals into peroxide radicals which do not react with $NO^{\cdot}$. Studies of kinetics of Scheme 35 have established that it has a 1 : 1 stoichiometry and is first order in both components. The rate of the hydroperoxide consumption is independent of whether the foreign radical $NO^{\cdot}$ is introduced into the system or not. Thus, the reaction is not a chain one. When the reaction is conducted in alcohol diluted with $H_2{}^{18}O$, the phosphorous-containing donor and hydroperoxide produce phosphine-oxide and alcohol not bearing the label. This means that Scheme 35 either does not produce free ions $HO^{\cdot}$ or does not exchange them with the medium. As Scheme 36 shows, the isotopic exchange should not take place: the ion-radical complex monomolecularly converts into the radical pair. The rate constant of Scheme 35 is independent of the solvent viscosity, whereas the rate constant of the $NO^{\cdot}$ consumption decreases as the viscosity of the medium rises. This decrease corresponds to the Stokes–Einstein law. This is typical of the reactions occurring in the solvent cage. Replacing benzene as a solvent by styrene or methylmetacrylate produces a peculiar effect on the reaction. These solvents add radicals by disrupting the double bond. The brutto rate of Scheme 35 in these solvents remains the same as in benzene, while the rate of $NO^{\cdot}$ decay somewhat increases because some more radicals leave the cage and pass into the solvent pool due to their affinity for the solvent molecules. So, it may be concluded that the reaction proceeds by a radical mechanism; however, the amount of radicals leaving the cage is small because they disproportionate inside the cage at such a high rate that even the rate of the radical addition to the double bond cannot compete with it.

This conclusion can be checked stereochemically. If hydroperoxide produces alcohol at the expense of the disproportionation of radicals not leaving the cage, the enantiomeric hydroperoxide should give the alcohol retaining the initial optical activity. And this is what actually happens.[118]

The ter Meer reaction. The reaction of ter Meer consists of the production of 1,1-dinitro compounds from 1-halo-1-nitroalkanes under the action of the alkali metal nitrite in basic medium[119] (Scheme 37).

$$RCH(X)NO_2 + NO_2^- + B: \longrightarrow RC(NO_2)_2^- + X^- + BH^+$$

Scheme 37.

$$CH_3CH(Cl)NO_2 + NO_2^- \rightleftharpoons CH_3C(Cl)=NOO^- + HNO_2 \rightleftharpoons$$

$$CH_3C(Cl)=NOOH + NO_2^- \longrightarrow CH_3C(NO_2)=NOOH \rightleftharpoons CH_3C(NO_2)_2^- + H^+$$

Scheme 38.

This reaction is used to synthesize 1,1-dinitroalkanes which find wide application as intermediate products in preparing drugs and biologically active substances.[119]

It was established thirty years ago that the reaction of 1-chloro-1-nitroethane with sodium nitrite in aqueous-alcohol medium is second order overall and first order in each reagent.[120] 1-Deutero-1-chloro-1-nitroethane reacts more slowly, i.e. the kinetic isotopic effect is observed. The reaction proceeds only in moderately alkaline media; in strongly alkaline media it does not take place. Only those heminal halo nitro compounds which carry hydrogen in the heminal node can undergo conversion. Based on these facts, Hawthorne[120] suggested the S_N2 substitution preceded by the isomerization into the acid form (Scheme 38).

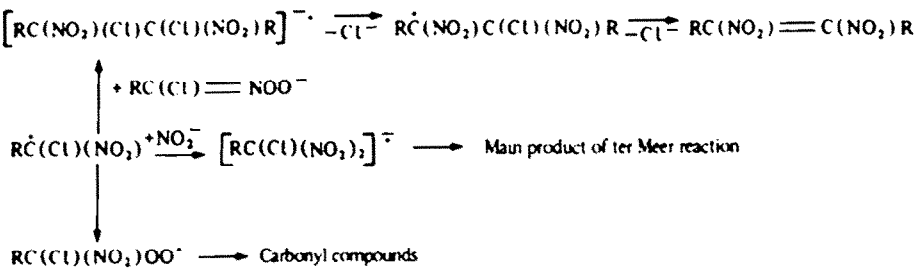
Recent research into the ter Meer reaction[119,121] has demonstrated that it has a chain ion-radical nature. Chain branching is attributed to the air oxygen, and a whole process of substitution in the aqueous-alkaline buffer medium is expressed by a complex (Scheme 39).

This scheme takes into account the data obtained by Hawthorne[120] and accords well with later results.[119] The mechanism shown in Scheme 39 has been supported as follows. In a moderately alkaline medium, the substrate ionization at stage 1 completely governs the kinetics of the reaction.[122] This agrees with the kinetic isotopic effect and the essential presence of hydrogen in the heminal node. For a chain ion-radical process to nucleate at stage 2, the reaction mixture should contain both the neutral substrate and the corresponding anion. This explains why the reaction shown in Scheme 39 does not occur with excess alkali: all the initial molecules convert into anions and electron exchange becomes impossible because there is no neutral substrate—acceptor of electrons - - in the reaction mixture. It has been revealed[122] that lack of alkali also decelerates the conversion: in the acetate-buffer solution the rate of the process drops and kinetic characteristics cease to obey the chain process laws. Under these conditions the reaction remains radical: the introduction of 4-oxy-2,2,6,6-tetramethylpiperidine-1-oxyl ($NO^{\cdot}$) inhibits the conversion. The acetate-buffer medium has a lower affinity for proton than the alkaline-buffer medium. This means that halonitrocarbanion forms in a lower yield. The anion is required not only for the nucleation (stage 1) but also for the development of the chain process (stage 10). Because of this the net rate of reaction decreases in the acetate-buffer medium, and the process ceases to be the chain one retaining, however, the radical nature (Scheme 39).

The presence of halonitro compounds incapable of producing carbanions, such as 2-chloro-2-nitropropane and trichloronitromethane, considerably increases the rate of chain nucleation in an

1. $CH_3CH(Cl)NO_2 + OH^- \longrightarrow CH_3C(Cl)=NOO^- + H_2O$
2. $CH_3C(Cl)=NOO^- + CH_3CH(Cl)NO_2 \longrightarrow CH_3\dot{C}(Cl)NO_2 + CH_3\dot{C}HNO_2 + Cl^-$
3. $CH_3\dot{C}(Cl)NO_2 + NO_2^- \longrightarrow CH_3C(Cl)(NO_2)_2^{\cdot-}$
4. $CH_3C(Cl)(NO_2)_2^{\cdot-} \longrightarrow CH_3\dot{C}(NO_2)_2 + Cl^-$
5. $CH_3\dot{C}(NO_2)_2 + CH_3C(Cl)=NOO^- \longrightarrow [CH_3C(NO_2)_2^-] + CH_3\dot{C}(Cl)NO_2$ etc.
6. $CH_3\dot{C}(Cl)NO_2 + O_2 \longrightarrow CH_3C(Cl)(NO_2)OO^{\cdot}$
7. $CH_3C(Cl)(NO_2)OO^{\cdot} + CH_3C(Cl)=NOO^- \longrightarrow CH_3C(Cl)(NO_2)OO^- + CH_3\dot{C}(Cl)NO_2$
8. $CH_3C(Cl)(NO_2)OO^- + H_2O \rightleftharpoons CH_3C(Cl)(NO_2)OOH + OH^-$
9. $CH_3C(Cl)(NO_2)OOH + CH_3C(Cl)=NOO^- \longrightarrow CH_3\dot{C}(Cl)NO_2 + CH_3C(Cl)(NO_2)O^{\cdot} + OH^-$
10. $CH_3C(Cl)(NO_2)O^{\cdot} + CH_3C(Cl)=NOO^- \longrightarrow CH_3C(Cl)(NO_2)O^- + CH_3\dot{C}(Cl)NO_2$

Scheme 39.



Scheme 40.

alkaline medium, pH 8.0.[122] These compounds accept electrons instead of non-ionized 1-chloro-1-nitroethane, the concentration of which is small at a high alkalinity.

The chain propagation (stage 3) involving the addition of the 1-chloro-1-nitroethyl radical to the nucleophilic nitrite ion has been supported by a number of works devoted to the radical interaction with anions.[123 126] Stage 4 presupposes that the anion-radical of 1-chloro-1,1-dinitroethane is only slightly stable and that it decomposes into the radical and the anion. This agrees with the results of investigations of the polarographic behaviour of heminal halonitroalkanes conducted with the help of ESR spectroscopy.[127] And finally, stage 5 of the one-electron oxidation of halonitrocarbanion with the 1,1-dinitroethyl radical is a well-known process. It regenerates the main particle, the chloronitroethyl radical, which acts as an initial point for the new chain.

In a moderately alkaline medium the ter Meer reaction proceeds through a considerable induction period; the kinetic curves are S-shaped; and the peroxide compounds and UV-irradiation accelerate the process.[121] Radical traps inhibit the reaction; this has been discussed above. All this points to the radical nature of the process. The rate of formation of active radical centres obeys the second-order equation in the total concentration of chloronitroethane introduced into the reaction. The reaction is first order in the non-ionized substrate and in the anion conjugated with it. The rate of the process is independent of the nitrite ion concentration. These proofs, essential to support mechanism 39, were obtained by two independent methods, which is important in the investigation of radical-chain reactions. The first method involves the determination of the induction period in the presence of 1-naphthol (the period is proportional to the naphthol concentration).[128] The other method consists in measuring the rate of inhibitor $(NO^{\cdot})'$ consumption; the intensity of the ESR signal decreases proportionally to the stable radical concentration.[129] Oxygen markedly decelerates reaction 39 and it loses its chain character.[121] This may serve as sufficient proof of stages 6–10.

The chain ion-radical mechanism 39 has been supported by a great number of facts and a thorough kinetic analysis. The ion-radical reactions of this type are well described by standard equations of chain-radical processes (with square-law chain termination).[119] This mechanism also explains the nature of side products: vic-dinitroethylenes, aldehydes and other carbonyl compounds. According to Schugalei,[130] the common predecessor of these products is the 1-chloro-1-nitroethyl radical which reacts with molecular oxygen and different nucleophiles present in the reaction mixture (Scheme 40).

The data of kinetics of parallel reactions permitted Schugalei[130] to calculate the rate constants of competing directions which are essentially the constants of the conversion selectivity. The analysis of the constants allowed the scientist to formulate the optimal conditions of the ter Meer synthesis of 1,1-dinitroalkanes. She suggested to conduct the reaction at concentrations of the initial reagents, 1-halo-1-nitroalkane and sodium nitrite, exceeding 1 mol l^{-1}. Then, the solubility of molecular oxygen in water is low (about 10^{-4} mol l^{-1}) and it would not affect the yield of the target product. An increase in the concentration of the nitrite ion promotes the ter Meer reaction. Increasing the concentration of alkali up to a certain limit also accelerates the reaction; beyond this limit, however, alkali produces an adverse effect on the reaction. Therefore, the optimal concentration of alkali is determined in each particular case. The authors[131] suggested the following solution to this problem: they recommended use of a strongly alkaline medium and sodium persulphate. 1-Halo-1-nitroethane does not react with sodium nitrite in 0.01 N aqueous sodium hydroxide (the substrate converts into the anion, and the system has no electron acceptor). The persulphate dianion performs the acceptor function, and 1,1-dinitroethane forms in 80–90% yield.[131] As is known,[123] the persulphate dianion oxidizes nitrocarbanions to the nitroalkyl radicals. The chain ion-radical nature of the reaction involving persulphate was proved with the help of the stable radical $(NO^{\cdot})'$[131] as described above. The rate of

1. $S_2O_8^{2-} + CH_3C(X)=NOO^- \longrightarrow CH_3\dot{C}(X)NO_2 + SO_4^{2-} + SO_4^{-\cdot}$

2. $SO_4^{-\cdot} + CH_3C(X)=NOO^- \longrightarrow CH_3\dot{C}(X)NO_2 + SO_4^{2-}$

3. $S_2O_8^{2-} + NO_2^- \longrightarrow NO_2^{\cdot} + SO_4^{2-} + SO_4^{-\cdot}$

4. $SO_4^{-\cdot} + NO_2^- \longrightarrow NO_2^{\cdot} + SO_4^{2-}$

5. $CH_3\dot{C}(X)NO_2 + NO_2^- \longrightarrow CH_3C(X)(NO_2)_2^{-\cdot}$

6. $CH_3C(X)(NO_2)_2^{-\cdot} \longrightarrow CH_3\dot{C}(NO_2)_2 + X^-$

7. $CH_3\dot{C}(NO_2)_2 + CH_3C(X)=NOO^- \longrightarrow \boxed{CH_3C(NO_2)_2^-} + CH_3\dot{C}(X)NO_2$ etc.

8. $CH_3\dot{C}(X)NO_2 + CH_3\dot{C}(X)NO_2 \longrightarrow CH_3C(X)(NO_2)C(X)(NO_2)CH_3$

9. $NO_2^{\cdot} + NO_2^{\cdot} \longrightarrow N_2O_4$

X = Cl, Br, J

Scheme 41.

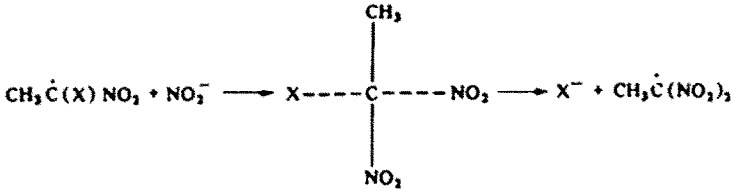
chain nucleation in the "persulphate" variant of the ter Meer reaction depends on concentrations of halonitroethane, nitrate and persulphate.[130] Changing the concentration of hydroxide and removing molecular oxygen from the reaction mixture practically do not affect the rate of the chain initiation. It has been established[131,132] that the persulphate dianion initiates chains while oxidizing both halonitrocarbanion and nitrite ion (Scheme 41).

Stages 1 and 2 represent the chain nucleation; stages 3 and 4 are the side process of the nitrate ion oxidation; stages 5–7 are the chain propagation; and stages 8 and 9 show the chain termination at the expense of radical dimerization. Stages 5 and 6 can probably be united into one stage (Scheme 42).

The anion-radical of 1-halo-1,1-dinitroethane is not a kinetically independent particle because of its extreme instability.[127] Therefore, the addition of the nitrite ion to the halonitroalkyl radical and the decomposition of the anion-radical of 1-halo-1,1-dinitroethane may proceed in one stage as shown in Scheme 42. As follows from the scheme, the effect of the leaving group—the halide ion—depends on the halogen affinity for the electron and the energy of the carbon–halogen bond disruption. The difference between the two energies increases in the series chlorine, bromine, iodine derivatives (2.4, 3.5 and 14.3 kcal/mol). The rate of process 42, i.e. stages 5 and 6, increases as compared with the rate of chain termination at stage 8 of mechanism 41. This, along with the alternative variant, has been considered by Schugalei *et al.*;[132] mechanism 42, however, is more illustrative. This mechanism unambiguously demonstrates that 1-fluoro-1-nitroethane is incapable of entering into the ter Meer reaction: the C—F bond in the anion-radicals of fluoronitroalkanes is extremely stable,[127] which excludes the possibility of the fluoride ion cleavage. The difference between the fluoride affinity for electron and the energy of the carbon–fluoride bond disruption is -30.5 kcal/mol.[133]

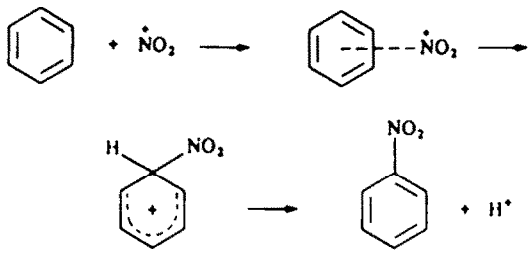
The above example is rather illustrative. It helps understand the peculiarities of the nucleophilic substitution reactions having the chain ion-radical mechanism and involving interaction of radicals with anions at the chain propagation stages. The example also demonstrates how the knowledge of kinetics and reaction mechanism can be used to find new ways of initiation and optimization of practically important reactions.

Nitration of aromatic compounds. These reactions involve substitution of the nitro group for hydrogen bonded to carbon of the aromatic nucleus. Nitration is one of the most important reactions of organic synthesis and, besides, it is widely used in industry. The investigations into the mechanism of



X = Cl, Br, J

Scheme 42.



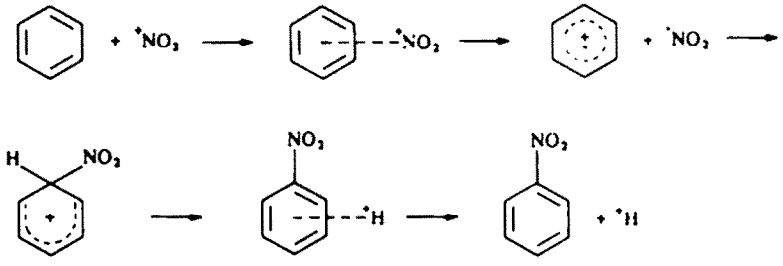
Scheme 43.

this reaction to find new ways of its optimization are still in progress. The studies of the ion-radical nature of the reaction can obviously help increase the selectivity of nitration, its yield and rate of formation of products of the desired structure. This research has been started only recently and, so far, has yielded no practically important results. The analysis of works on the ion-radical identification of nitration seems beneficial even now because the methodological approaches to the problem are abundant.

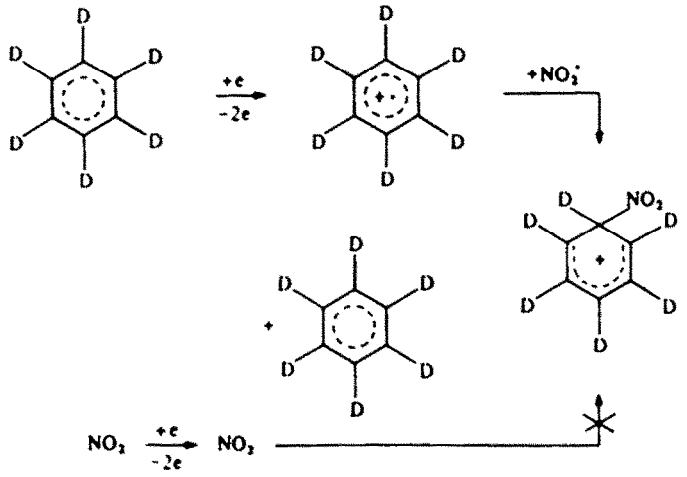
The ion-radical pathway of nitration presupposes that the aromatic compound and the nitrating agent enter into the oxidation–reduction reaction. Products formed in the redox interaction couple at subsequent stages. Let us consider the nitration of benzene[134 136] as an example. The substitution proceeds through stages given in Scheme 43.[137]

The process starts with the formation of the π-complex, which corresponds to a partial charge transfer. Then, the π-complex rearranges into the σ-complex, and the light particle, proton, cleaves. Within the framework of the perturbation theory[137] this is formulated as the formation of the transition state between "the π-system perturbation and perturbation of a particular carbon". The perturbation theory, however, does not consider electron transfer as a separate stage.[137] As the reagent approaches the bond of the substrate being attacked, the energies of the lowest unoccupied molecular orbital (LUMO) and the highest occupied molecular orbital (HOMO) change.[138] The distance between molecules at which one-electron transfer becomes possible depends on the degree of perturbation. When the distance is great the compounds produced at this step pass into the solvent pool, and when it is small they recombine inside the solvent cage.[138] In the benzene nitration by the cation NO_2^+, an electron may be transferred if the distance between the reagents is 1.5–2.5 Å.[139] This distance is close to that usually assumed in calculations of the electrophilic nitration.[139] The quantum-chemical studies[135] demonstrate that the nitronium cation LUMO has an energy of -11.0 eV and the benzene HOMO, an energy of -9.24 eV. This makes another step of nitration theoretically possible, namely electron (unit charge) transfer from the benzene HOMO to the nitronium cation LUMO; this step is given in a general scheme (Scheme 44). Particles forming the biradical pair may unite to produce the σ-complex.

It is quite evident that upon their formation, radical $NO_2^{\cdot}$ and cation-radical $C_6H_6^{+\cdot}$ will tend to react with each other. This tendency shows itself regardless of the distance between the radical and cation-radical, but the distance determines the factor affecting the orientation in one or another substitution reaction. Perrin[29] reports that at great distances the orientation depends on the density of the unpaired electron in one or another position of the ion-radical. At relatively small distances the orientation at substitution depends on the position that occupies carbon capable of forming the most stable bond in the production of the σ-complex.



Scheme 44.



Scheme 45.

Two main conclusions follow from what has been said above:

1. The step of one-electron transfer included in the mechanism of reaction does not argue against the commonly accepted idea of nitration, rather it makes it more exact and applicable for making judgements as to the selectivity of the reaction.

2. There is doubt, however, that the step of electron transfer is essential in absolutely all cases of nitration. It is difficult to suppose that an electron is transferred, for example, in nitration of dinitrobenzene to the trinitro derivative: despite that the probability of oxidation of dinitrobenzene into the cation-radical under the effect of the nitrating agent is small nitration proceeds rather effectively.

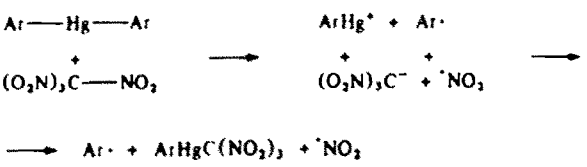
Experiments yield data on the identification of the ion-radical mechanism of nitration of benzene or compounds more easily oxidizable than benzene. The reactions taking place in the gas and liquid phases will be discussed separately.

Nitration in the gas phase. Mass-spectrometric studies yield the most convincing results. The ionization of perdeuterobenzene and nitrogen dioxide at a low pressure produces a σ-complex $(C_6D_6NO_2)^+$.[140] The origin of this complex was studied by means of ion-cyclotron resonance.[140] As a result, the authors[140] have found out that the rate of the σ-complex formation depends not on the rate of generation of cations NO_2^+ but rather on that of cation-radicals $C_6D_6^{+\cdot}$. Thus, particles $C_6D_6^{+\cdot}$ and $NO_2^{\cdot}$ and not the pair C_6D_6 and NO_2^+ are the predecessors of σ-complex $(C_6D_6NO_2)^+$ (see Scheme 45).

Otherwise, the reaction takes the route shown in Scheme 44 and not the route given in Scheme 43. Mass-spectrometric investigations conducted at a high pressure[141] yielded the same results. The ionization of a gaseous mixture of C_6H_6, NO_2, He and Ar produces cation-radical $C_6H_6^{+\cdot}$. While interacting with the radical $NO_2^{\cdot}$ the cation-radical converts into the complex $(C_6H_6NO_2)^+$. The complex was identified as follows. Schmitt *et al.*[141] ionized a mixture of vapours of perdeuterobenzene, nitrogen dioxide and tetrahydrofuran. The latter was used as a base capable of detaching a deuteron. It was established that deuteron is transferred to the base not from the ion $(C_6D_6)^{+\cdot}$ but rather from the ion $(C_6D_6NO_2)^+$. This confirms the σ-complex structure of ion $(C_6D_6NO_2)^+$, because only the σ-complex may carry deuterium, the acidity of which is sufficient to transfer deuterium to tetrahydrofuran. Schmitt *et al.*[141] obtained similar results for toluene and *p*-xylene.

Thus, under the conditions of gas-phase ionization, nitration of benzene and its homologues obviously proceeds by Scheme 44. Further studies into the mechanism of gas-phase nitration will reveal whether these conditions are far from or close to the conditions of purely chemical reactions. At present we should draw attention to studies[142,143] which demonstrate that cation-radicals of aromatic compounds react in the gas-phase with alkylnitrites releasing the alkoxy radicals and capturing nitrogen dioxide. The mechanism of the gas-phase nitration is probably common to many reactions.

Nitration in the liquid phase. Liquid phase due to solvent effects may markedly change the stability and reactivity of the participants of an ion-radical reaction. However, the organic, and, in particular, aromatic substrates oxidize in solutions at fairly low potentials. The nitronium ion which directly or indirectly participates in aromatic nitration reduces to nitrogen dioxide extremely easily. This means



Scheme 46.

that the ion-radical mechanism may be operative in the liquid phase too. It has been demonstrated that nitronium cation, for example, causes one-electron oxidation of naphthalene,[144] N,N-dimethylaniline, or aromatic derivatives of dioxane and dihydropyrasoline[145] in organic solvents.

It is quite evident that in solution one-electron oxidation also depends on the reducing properties of one or another substrate as regards the nitronium cation. The activity is determined by both the nature of a substrate and the effect of a solvent. Benzene, for example, reduces cation NO_2^+ in the gas phase and fails to do so in the liquid phase. This may be concluded from the absence of the CIDNP effect in the ^{1}H-NMR spectrum corresponding to the liquid phase nitration of benzene with NO_2BF_4.[146]† The reaction, according to ^{1}H-NMR data, quickly proceeds through the stage of σ-complex formation, and, hence, the absence of polarization could not be attributed to time after radical–cation-radical coupling.

It should be noted that the reactivity of radical $NO_2^{\cdot}$, which originates from the cation NO_2^+ upon one-electron reduction, decreases in the liquid phase. The interaction between the aryl derivatives of tin, magnesium and mercury and tetranitromethane in sulpholane supports the above statement.[147] To illustrate this, the reaction of biaryl mercury with tetranitromethane[147] produces at the intermediate stage the aryl and $NO_2^{\cdot}$ radicals (Scheme 46).

The aryl radical, although it is highly active, does not couple with radical $NO_2^{\cdot}$. The solvent molecule cleaves hydrogen much more rapidly and produces aromatic hydrocarbon. Radical $NO_2^{\cdot}$ is most probably stabilized as dinitrogen tetroxide and is consumed in side oxidation reactions. The reaction of tetranitromethane with aryl derivatives of tin, magnesium and mercury yields radicals Ar$^{\cdot}$ and $NO_2^{\cdot}$ which do not react with each other in the liquid medium.

The nature of the radical acceptor obviously affects the activity of radical $NO_2^{\cdot}$ in the liquid phase: cation-radicals of some heteroaromatic compounds easily trap radicals of nitrogen dioxide. Thus, the dibenzo-*p*-dioxane cation-radical[145] and the phenothiazine cation-radical[148] capture $NO_2^{\cdot}$ and yield the same nitro products as the nitration of neutral heterocycles by nitric acid.[145,148]

To conclude, the nitronium cation in the liquid phase sometimes forces the substrate to undergo one-electron oxidation and form the nitrogen dioxide radical and the substrate cation-radical. Specially prepared stable cation-radicals of a number of substrates combining with the nitrogen dioxide radical give the same nitro compounds as the standard electrophilic nitration. These data are necessary but not sufficient to prove the ion-radical mechanism of nitration: it is to be proved that these conversions take place on the main pathway of the electrophilic substitution. To get data in support of this assumption, researchers referred to electrochemical modelling and other methods of identification of ion-radical reactions.

A number of studies[29,149,150] are devoted to electrochemical modelling of nitration of aromatic substrates. Perrin[29] described the electrolysis of a mixture of naphthalene and dinitrogen tetroxide in acetonitrile at the platinum anode. By controlling the potential Perrin made naphthalene undergo one-electron oxidation without any oxidation of the nitrogen dioxide radical to the nitronium cation. The electrolysis yields α- and β-naphthalene in the ratio 9 : 1. Nitrating naphthalene with a mixture of nitric and sulphuric acids in acetonitrile gives a mixture of α- and β-naphthalenes of the same composition. This is an argument in support of the electrophilic nitration of naphthalene proceeding by the cation-radical mechanism. Perrin[29] did not report the electric charge per mol of naphthalene. So, it cannot be concluded whether nitronaphthalene converts into the cation-radical at the anode or the anodic oxidation and the nitration of the initial naphthalene proceed concurrently and independently of one another. It is clear that the radical $NO_2^{\cdot}$ attacks primarily the α-position of naphthalene without the oxidation of naphthalene into the cation-radical. Position α features the highest radical unsaturation.

† Later a case will be discussed when the ^{1}H-NMR spectrum shows no CIDNP effect, while the ^{15}N-NMR spectrum visualizes a considerable polarization.

This means that the same proportion of products of the electrophilic and oxidative (anodic) nitration is not a sufficient proof of the ion-radical nature of nitration.

Olah *et al.*[149] nitrating naphthalene with dinitrogen tetroxide in the presence of the oxidizer, cerium ammonium nitrate, also produced at ambiguous results. The oxidative and electrophilic nitration may proceed under these conditions concurrently: the ratio of α- and β-nitronaphthalenes is 16:1 and not 9:1 as reported by Perrin.[29] Eberson and Radner[150] conducted the oxidative nitration of naphthalene at −45° in dichloroethane saturated with dinitrogen tetroxide and containing electrolyte Bu_4NPF_6. Naphthalene under these conditions converts into its cation-radical which combining with the unreacted naphthalene produces a crystalline salt $(C_{10}H_8)_2^{+\cdot}PF_6^-$. When the mixture is heated to −25° the nitration starts and produces a mixture of α- and β-nitronaphthalenes in the ratio 40:1. The nitration probably involves the cation-radical and neutral components of dimeric ion $(C_{10}H_8)_2^{+\cdot}$. Therefore, the nitration may proceed by two parallel pathways. The α/β ratio in nitrating neutral naphthalene by dinitrogen tetroxide in dichloroethane (without the oxidizer) is 15:1.[148] This ratio differs from that reported by Perrin[29] and so refutes his statement. Moreover, Eberson *et al.*[30] have demonstrated that the anodic nitration of naphthalene under the conditions of Perrin's experiment is catalyzed by the anodically generated acid. The rate of nitration decreases as the temperature drops.[30] By contrast, ion-radical reactions are only slightly sensitive to temperature changes.

Thus, nitration of naphthalene under the conditions of electrochemical modelling is predominantly a homogeneous process in which the cation-radical part of the substrate does not play the decisive role. Therefore, the method is probably unsuitable for the identification purposes.

The reaction between N-methylphenoxazine and tetranitromethane in acetic acid was studied spectroscopically: the reaction gives 3-nitro-N-methylphenoxazine in an 80% yield.[151] As may be judged by the intensity of the corresponding bands in the visible region of the absorption spectrum, the reaction has two stages. The first involves one-electron transfer: 90% of the substrate converts into the cation-radical over a period of two minutes, the cation-radical being characterized by the ESR spectrum. The second stage converts the cation-radical into the product of nitration. The process lasts for two hours. The family of spectra recorded in the course of the reaction have a well defined isosbastic point. Morkovnik *et al.*[151] came to the conclusion that 3-nitro-N-methylphenoxazine is produced from the cation-radical of N-methylphenoxazine. The cation-radical of phenoxazine is generated together with the anion-radical of tetranitromethane. If we assume that this anion-radical gradually decomposes into the trinitromethyl anion and radical $NO_2^{\cdot}$, we may come to a scheme analogous to that describing nitration of benzene.[45] The authors,[151] however, do not report the scheme of the reaction and say nothing of the fate of trinitromethane upon completion of the N-methylphenoxazine nitration. The work of Isaacs and Abed[152] is much more valuable in this respect.

They studied the mechanism of nitration of aromatic compounds with tetranitromethane and established that tetranitromethane nitrates the nitrogen-carrying heterocycle at nitrogen.[152] This produces a mild nitrating agent which acts as a carrier of ion NO_2^+. Then, the process may proceed in the same way as has been discussed for the nitration with the nitronium cation. It is important to note that in this case the products of nitration should accumulate at a reduced rate; this has been mentioned above.

Nitration reactions considered up to now are simple in the sense that nitrating agents directly participate in one-electron oxidation of a substrate (or the substrate is used in the ion-radical form). The nitration with nitric acid is a more complex reaction. This reaction is extremely important as it most closely approximates the industrial process. The main difficulty is to identify the one-electron oxidizer in the system substrate–nitric acid. This oxidizer may be the nitronium cation generated from nitric acid at a proper acidity of the medium. As has been found, the interaction of aromatic compounds with nitric acid produces cation-radicals also under the conditions excluding the participation of the nitronium cation. These conditions are, say, 80% acetic acid at small concentrations of HNO_3.[153] Nitric acid reduced by an aromatic compound may produce a complex equilibrium mixture of low-valency nitrogen compounds which have pronounced oxidative properties. Giffney and Ridd[154a] studied the mechanism of nitration of N,N-dimethylaniline with nitric acid in aqueous sulphuric acid. They adduce a number of arguments in support of the stage which involves the autocatalytical oxidation of N,N-dimethylaniline by the nitronium cation to produce the cation-radical.

It is common knowledge that nitric acid used in nitration partly converts into nitrous acid at the expense of oxidation of the aromatic substrate. Nitrous acid in the presence of a water-removing agent (H_2SO_4) forms the nitrosonium cation. It is assumed that cation NO^+ acting on the substrate gives the

nitroso compound which is oxidized by the nitric acid into the nitro derivative:

$$ArH + NO^+ \xrightarrow[H^+]{} ArNO \underset{-HNO_2}{\overset{+HNO_3}{\longrightarrow}} ArNO_2.$$

The nitration, however, may proceed by another scheme taking account of the catalytic action of the nitrosonium cation:

$$ArH + NO^+ \rightleftarrows ArH^{+\cdot} + NO^{\cdot};$$

$$NO^{\cdot} + NO_2^+ \rightarrow NO^+ + NO_2^{\cdot};$$

$$ArH^{+\cdot} + NO_2^{\cdot} \rightarrow [Ar(H)NO_2]^+ \xrightarrow[-H^+]{} ArNO_2.$$

This scheme is based on the following assumptions: the substrate should be oxidized easily or, at least, relatively easily; the composition of products should be independent of the nitric acid concentration; and the reaction should be zero order in nitric acid. So, this should be a chain or a branched-chain reaction. These peculiarities have been confirmed on the example of nitrating the following compounds: dibenzo-*p*-dioxane,[145] 1,2,3-trimethoxy-5-nitrobenzene,[155] N,N-dimethylaniline,[154a] and 4-nitrophenol.[154b] Nitration of N,N-dimethylaniline produces only *meta* and *para* nitro derivatives; when N,N-dimethylaniline is nitrated in the *para*-position the reaction autoaccelerates, when it is nitrated in the *m*-position, it does not.[154] When N,N-dimethylaniline is nitrated with nitric acid enriched (95%) with ^{15}N, the ^1H-NMR spectrum shows no abnormal behaviour, while the ^{15}N-NMR spectrum visualizes a considerable polarization.[156] It is of interest that the abnormal polarization of nuclei ^{15}N is revealed only in the case of N,N-dimethyl-*p*-nitroaniline; the substitution into the *meta* position produces no polarization.[156] The authors[156] do not explain the difference between the *para* and the *meta* nitration of N,N-dimethylaniline. It is clear, however, that the nitro compound obtained by a catalytic process has a radical (cation-radical) origin.†

Cation NO^+ as an oxidizer is many times weaker than cation NO_2^+. This conclusion is drawn from the electrochemical data.[29,157] At the proper acidity of the medium, however, cation NO^+ is produced more easily than cation NO_2^+.[158] In the case of substrates liable to oxidation it is the nitrosonium cation that controls the reaction. This is illustrated in the example of reactions of heteroaromatic compounds with nitric acid in perchloric acid.[159] One-electron oxidation of heterocycle (Het) proceeds through a well defined induction period and releases nitrogen oxide. The stoichiometry of the process follows the equation

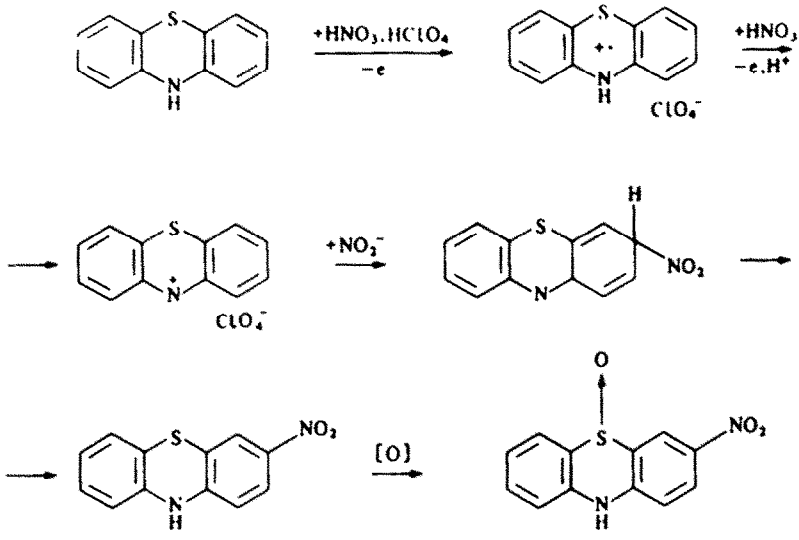
$$3(Het) + HNO_3 + 3H^+ \rightarrow 3(Het)^{+\cdot} + NO^{\cdot} + 2H_2O.$$

The products of the reaction were separated and characterized.[152] The interaction of the substrate with the nitrosonium cation is one of the stages of the process. Another stage is the oxidation of nitrogen oxide with the nitronium cation or nitric acid[160] leading to the regeneration of the nitrosonium cation in an acidic medium. This self-accelerates the reaction and autocatalyzes it.

The reaction is also complex with respect to the substrate. Thus, the cation-radical of phenothiazine is not a direct predecessor of the nitro derivative. Under the action of excess nitric acid it undergoes further one-electron oxidation into the phenoazthionic ion.[161] The latter is attacked by the nitrite ion of nitrous acid which is produced when the organic substrate reduces part of the nitric acid. The final product is 3-nitrophenothiazine-S-oxide (Scheme 47).

In conclusion it may be said that although the electrophilic aromatic nitration is the typical reaction for a wide range of substrates, it cannot be thought of as a process having the same mechanism in all cases. However, under proper conditions of the medium the ion-radical mechanism becomes decisive for substrates liable to one-electron oxidation and capable of producing stable cation-radicals. The examples cited in this section demonstrate that this mechanism can be identified with the help of contemporary methods. The researchers still face the problem of finding out how broad the range of nitration involving one-electron transfer is. The problem is extremely complex because rapid conversions of aromatic cation-radicals may mask the ion-radical nature of these reactions and create the illusion of their non-radical behaviour. Therefore, the identification of ion-radical conversions remains the

† At least 20% of nitration of 4-nitrophenol with HNO_3 in AcOH proceeds through the generation of $^{\cdot}NO_2$. This radical enters into the ipso-position of 4-nitrophenol.[154b]



Scheme 47.

problem topical for organic chemistry. The solution of this problem will certainly open up new venues in the optimization of many industrially important reactions.

III. INITIATION OF ION-RADICAL CONVERSIONS

1. *Effect of functional groups*

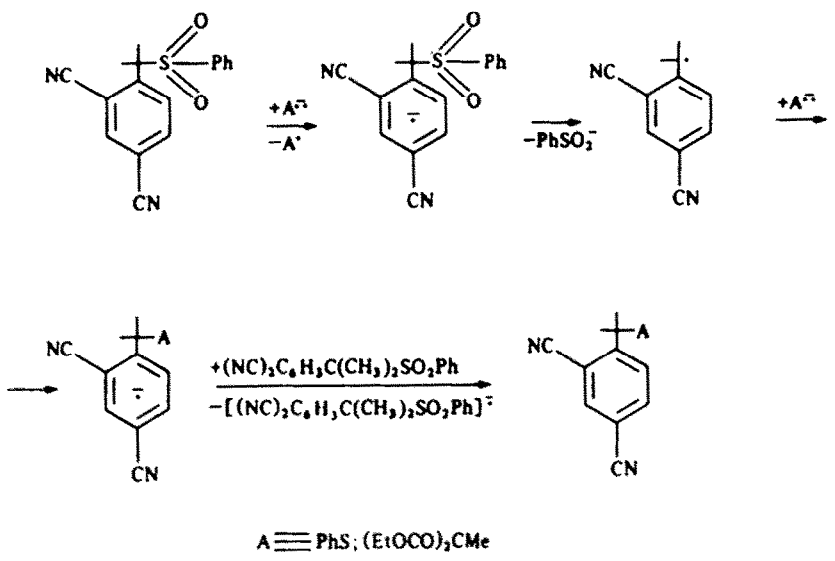
The functional groups in a molecule determine to a considerable degree whether it can exist in the ion-radical form. The effect of substituents on the properties of the ion-radical molecule has not been developed adequately. The main problem is to find out what groups should be introduced into the molecule to make it react by the ion-radical mechanism. It may be said only that these groups should, first, impart pronounced acceptor or donor properties to the molecule and, second, stabilize the ion-radical produced. In the case of anion-radicals these groups are the nitro, cyano, carbonyl and sulphonyl, and trifluoromethyl when more than one group is present in the molecule. This list, however, is not final; it will be completed as the research yields new data. In the present state of the art such strong donors as the methoxy and amino groups are considered as stabilizers of cation-radicals. Cation-radicals are more reactive than anion-radicals, and the cation-radical centre should be shielded to stabilize them. Therefore, scientists prefer to use donor substituents loaded with different fragments, say, N,N-dialkylamino group or vinyl group carrying alkyl radicals, to simple donors.

We want now to show on the example of specific reactions how the anion-radical pathway is realized in the series of sulphonylnitrile derivatives, how the introduced group affects the stability of the anion-radical product, and how spin density is localized in the vicinity of the leaving group.

o,p-Dicyano-α-phenylsulphonylcumene reacts with sodium thiophenolate in DMF and produces *o,p*-dicyano-α-phenylthiocumene (Scheme 48).[162] A similar result is obtained with the potassium salt of diethyl malonate as a reagent and with the same substrate.[162]

Irradiation accelerates the reaction, and the substitution product is formed in a 70–80% yield. Acceptors of radicals (di-t-butylnitroxyl) or acceptors of electrons (*m*-dinitrobenzene) completely inhibit the substitution even if present in the reaction mixture in small amounts. A reaction of type 48 does not take place when the initial α-phenylsulphonylcumene bears no cyano groups. Hence, the cyano group directs the reaction via the ion-radical pathway. Even one cyano group if it is in the *para*-position of the aromatic nucleus can initiate the reaction. Like the nitro group, the cyano group promotes the formation of the anion-radical, which originates upon one-electron transfer from the thiophenolate or malonate ion to the substrate (Scheme 48).

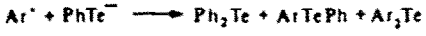
Thus, the substrate molecule should carry groups which could promote the formation and stabilize the produced ion-radical. The reagent molecule should give or trap an electron, otherwise the substrate would not be able to form an anion- or cation-radical. A radical produced from an ion-radical after the leaving group has cleaved from it should posses certain electrophilicity with respect to the anionidic



Scheme 48.

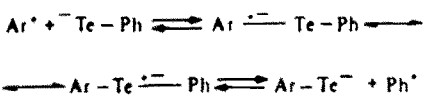
reagents and nucleophilicity with respect to the cationidic reagents. For example, radicals preserving electron-acceptor groups should add negatively charged reagents more easily than radicals devoid of such groups. For a chain process to develop, the molecule of the initial substrate should enter into electron transfer more facilely (be more acceptor or more donor) than the product molecule. Only in this case may the spin density move from the product ion-radical to the initial uncharged substrate. And finally, the reagent should effectively capture the substrate radicals.

In the series of the halkogenide anions of the type PhZ(Z = O, S, Se, Te), for example, thiophenolate ions effectively trap aryl radicals, anions of phenyl selenide are twenty times less active, and phenolate anions are absolutely inactive. The reaction of aryl radicals with phenyltelluride ions proceeds in the abnormal fashion: the products are asymmetrical and symmetrical tellurides[163] (Scheme 49).



Scheme 49.

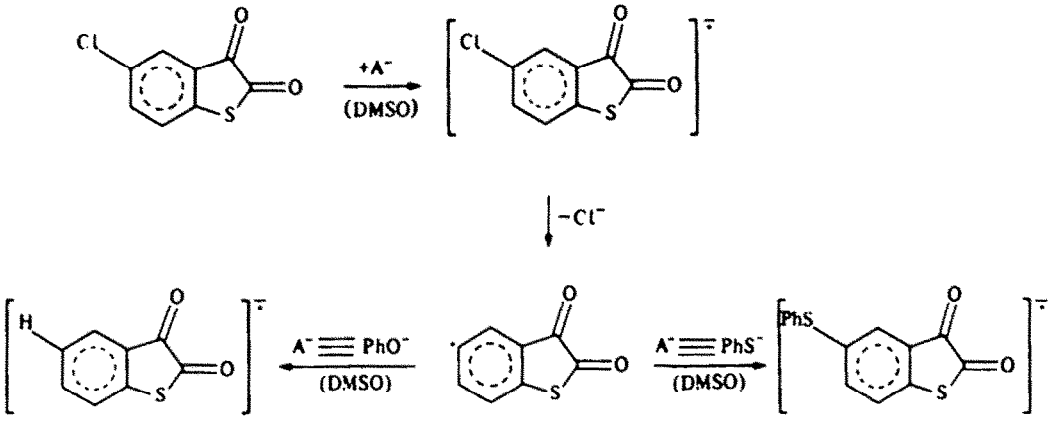
As molecular orbital calculations show,[164,165] the energy levels for pairs Ar· + TePh and ArTe⁻ + Ph· are equal. This makes possible the decomposition of the intermediate anion-radical by Scheme 50.



Scheme 50.

A number of reactions demonstrate a high activity of the phenylthiolate ion in trapping aryl radicals and the inability of the phenolate ion to do so. Thus, the phenylthiolate anion acting on 5-chloro-2H,3H-benzo[b]thiophenedione-2,3 produces the substitution product (in the anion-radical form), while the phenolate anion initiates only the reductive dechlorination[166] (Scheme 51).

To disrupt the C—Cl bond at position 5 of the substrate anion-radical, spin density of this bond should be increased. However, if spin density at carbon-carrying chlorine is too great, the initial chlorine-containing anion-radicals dimerize instead of cleaving the chloride ion. Thus, in the isomeric 6-chloro-2H,3H-benzo[b]thiophenedione-2,3 anion-radical, electron density at carbon-6 is five times greater than at carbon-5, and the dimerization proceeds much more rapidly than the cleavage of the C—Cl bond.[167]



Scheme 51.

2. *Effect of magnetic field*

The effect of a magnetic field on the rate of ion-radical reactions has a physical background.[168] It can be explained not by a change in the energy of reactions in a magnetic field but rather by the effect of the field on the probability of elementary chemical acts. The effect of a magnetic field on the processes involving radicals has been thoroughly discussed by Sagdeev *et al.*[169] Increasing the magnetic field strength from 0.5 Oe to 20,000 Oe considerably changes the ratio of products resulting from the interaction of pentafluorobenzyl chloride, $C_6F_5CH_2Cl$, and n-butyllithium, BuLi (Scheme 52).

$$C_6F_5CH_2Cl + BuLi \longrightarrow C_6F_5CH_2Cl^{\cdot-}\cdot Li^+ + Bu^{\cdot};$$

$$C_6F_5CH_2Cl^{\cdot-}Li^+ \longrightarrow C_6F_5CH_2^{\cdot} + LiCl;$$

$$C_6F_5CH_2^{\cdot} + Bu^{\cdot} \longrightarrow C_6F_5CH_2Bu;$$

$$C_6F_5CH_2^{\cdot} + C_6F_5CH_2^{\cdot} \longrightarrow C_6F_5CH_2CH_2C_6F_5,$$

$$Bu^{\cdot} + Bu^{\cdot} \longrightarrow Bu{-}Bu$$

Scheme 52.

The authors do not consider a chain process represented by Scheme 53 but note that in high magnetic fields the yield of the substitution product, $C_6F_5CH_2Bu$, rises considerably.[169] This demonstrates that a magnetic field increases the recombination of radicals $C_6F_5CH_2^{\cdot}$ and $Bu^{\cdot}$ giving the product of formal substitution.

3. *Effect of light*

Endicott and Ramasami[170a] prove that electron excitation of reacting molecules accelerates the reactions involving electron transfer. Having absorbed a quantum of light a molecule becomes excited. Upon photoirradiation an electron in donors occupies a higher orbital. The energy of "external" electrons increases, and so the donating properties of the molecule rise, in other words, electron transfer to an acceptor becomes more probable. The acceptor molecule upon photoirradiation demonstrates the same change in the electronic configuration. Reactions may be photoinitiated when the difference between the ionization potential of a donor and the affinity to electrons of an acceptor is great. When

$$C_6F_5CH_2^{\cdot} + Bu^-Li^+ \longrightarrow C_6F_5CH_2Bu^{\cdot-}\cdot Li^+;$$

$$C_6F_5CH_2Bu^{\cdot-}\cdot Li^+ + C_6F_5CH_2Cl \longrightarrow$$

$$C_6F_5CH_2Bu + C_6F_5CH_2Cl^{\cdot-}\cdot Li^+$$

Scheme 53.

the irradiation wavelength is chosen correctly, only donors may be excited and the above-mentioned difference increases. This is often done by using irradiation in the spectral region corresponding to a charge transfer of a complex produced by a donor and an acceptor prior to irradiation.[170b] Ion-radicals produced in this way may either exist upon de-excitation or regenerate the initial uncharged molecules. Concurrently, excited molecules may undergo numerous chemical conversions: the energy absorbed in irradiation is spent to disrupt bonds, rearrange molecules, isomerize or dimerize them, etc. Irradiation also affects the products of interaction of ion-radicals with one another. Despite the fact that the picture is rather complex, the mechanism of photo-initiated reactions can be as reported in this review[164] (see also references to this review). According to this approach, an ion-radical reaction between a substrate and a nucleophile is initiated by light. The substrate produces the anion-radical, which decomposes as shown, say, in Scheme 48. Then, the produced radical—the residue of the substrate—interacts with the second molecule of the nucleophile. The product of the reaction is in the anion-radical form and it starts another cycle of the substrate conversion into the anion-radical at the expense of electron transfer.

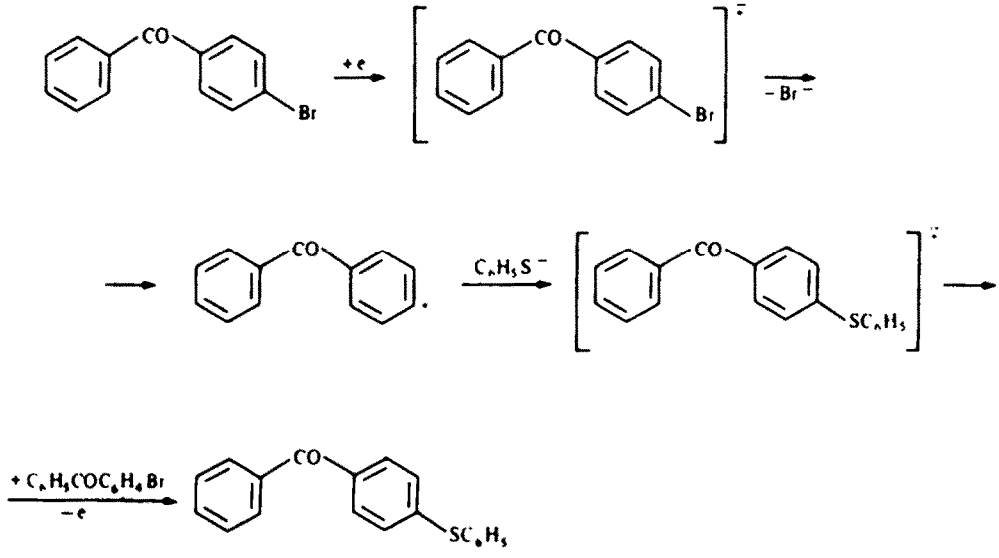
4. *Electrochemical effect*

We cite now two examples demonstrating that thioarylation may be facilitated electrochemically.

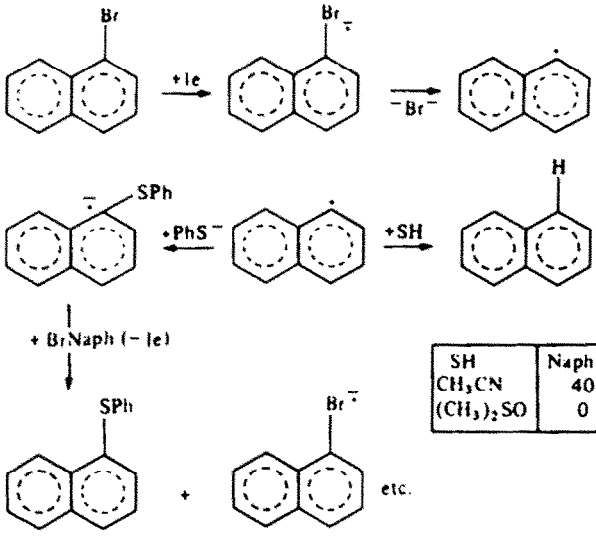
The nucleophilic substitution of bromine by the thiophenolate ion in 4-bromobenzophenone proceeds under extremely rigid conditions.[171] When a difference in electrical potentials is set up, the reaction goes easily and gives products in a high yield (80%); it is sufficient to set up the potential difference necessary to ensure the formation of the substrate anion-radical (the potential and current passed through the solution were strictly controlled). Then, a chemical reaction takes place in the volume of solution and yields 4-phenylthiobenzophenone (Scheme 54).

1-Bromonaphthalene does not react with thiophenolate.[172-174] However, when current is passed through a solution containing 1-bromonaphthalene, the tetrabutylammonium salt of thiophenol and dimethylsulphoxide (DMSO), 1-phenylthionaphthalene is produced quantitatively; when the reaction is conducted in acetonitrile, it gives naphthalene above all. To this end it is sufficient to set up the potential difference corresponding to the initial current of the reduction wave of 1-bromonaphthalene to 1-naphthyl radical. The difference in electric charge is rather remarkable: in the absence of thiophenolate, bromonaphthalene reduces accepting two electrons per molecule, whereas in the presence of thiophenolate, the product of substitution forms quantitatively accepting two electrons per ten molecules of bromonaphthalene. The reaction with the thiophenolate ion is catalyzed by current and proceeds through the following stages (see Scheme 55):

(i) the formation of the 1-bromonaphthalene anion-radical which rapidly converts into the 1-naphthyl radical; (ii) the interaction of naphthyl radicals with thiophenolate. The process goes in the



Scheme 54.



SH	Naph. %	PhS – Naph. %
CH_3CN	40	32
$(CH_3)_2SO$	0	100

Scheme 55.

electrode space and competes with the formation of the unsubstituted naphthalene at the expense of the reaction of radicals with the solvent molecules (SH); (iii) the oxidation of the product anion-radicals by the substrate neutral molecules (in the volume of solution); (iv) the chain propagation involving the decomposition of the 1-bromonaphthalene anion-radical.

In addition to bromonaphthalene, bromobenzophenone (Scheme 54) or bromobenzonitrile[172] (that is compounds carrying not only bromine but also other electrochemically active groups) may be used as substrates. Along with the thiophenyl, the thiomethyl or thio-t-butyl groups are used as substituting fragments. The yields of substitution products are high (60–95%), and one electron is consumed per 20–30 molecules of the substrate. Reactions proceed at room temperature and do not go at all when the potential difference is not set up.

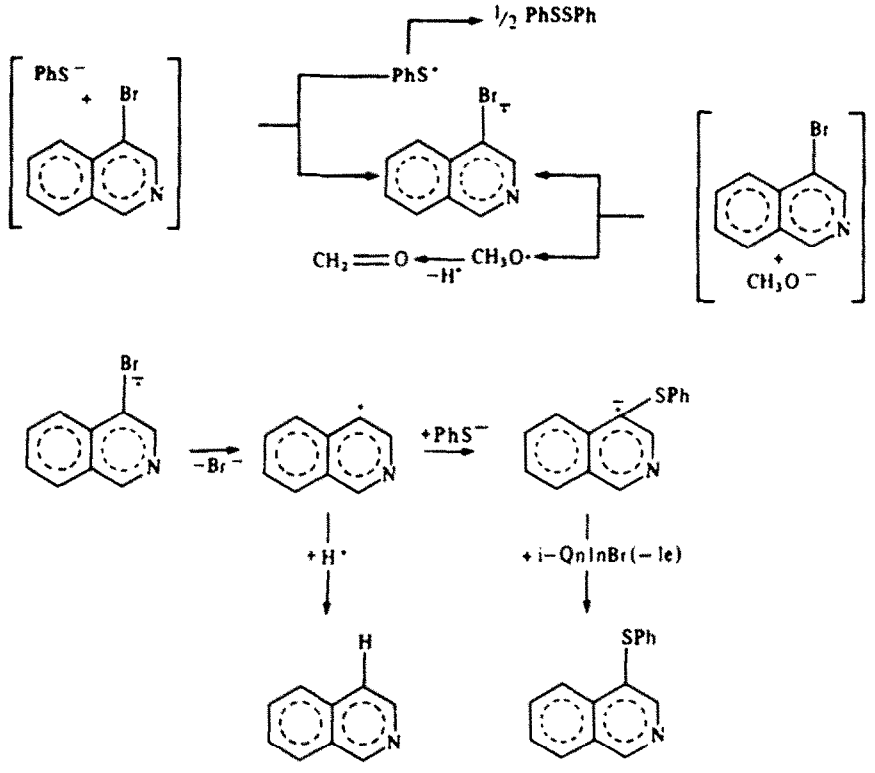
The electrochemical entrainment of ion-radical reactions has the following peculiarities:[173,174]

(i) the reactions are highly selective and give products in high yields. They need no activation of the substrate by electron-accepting substituents; (ii) the initial substrates have a greater affinity for electron than the products of substitution. Therefore, the substrate easily accepts excess electron belonging to the product anion-radical. This creates conditions necessary for a chain process to take place, and the reaction becomes catalytic with respect to current efficiency; (iii) the electrode potential may be such as to initiate the substrate substitution without reducing the product of substitution; (iv) the undesired conversion of aryl σ-radical into the unsubstituted hydrocarbon at the expense of the interaction with a solvent may be inhibited. To this end the solvent should be chosen in such a way that it possesses a sufficient electroconductivity in the presence of a supporting electrolyte but should not cleave hydrogen.

Thus, when the reaction between 1-bromonaphthalene and $PhSNBu_4$ is conducted in acetonitrile, naphthalene and 1-phenylthionaphthalene are produced in equal amounts, GLC reveals that phenylthionaphthalene is produced in DMSO quantitatively, while naphthalene is not formed at all.[172] This accords well with the literature data;[175,176] acetonitrile donates hydrogen much more easily than DMSO. According to Pinson and Savéant,[172] the $S_{RN}1$ reaction is 100% selective in the substitution product, and the competing interaction of the α-naphthyl radical with the solvent does not take place at all. Helgee and Parker[177] opposed this conclusion. To support their data Pinson and Savéant checked the results by analysing the reaction products polarographically.[174] As a result, the selectivity in the substitution products is only 80% and not 100% as considered before. This, too, is sufficient for synthetic purposes.

5. *Chemical effect*

This problem has been thoroughly studied.[178] Therefore the most fundamental examples will suffice, including those which remained outside the scope of the review. The main contribution to the

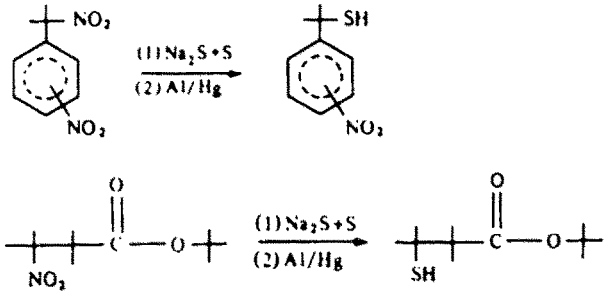


Scheme 56.

problem has been certainly made by an American scientist, Kornblum.[179] He studied nucleophilic substitution in the series of cumene derivatives; one of such reactions is given in Scheme 48. The anion-radical of the cumene derivative produces in the course of the reaction the cumyl radical. Kornblum thought that this radical may be trapped not only by those nucleophilic ions the part of which was spent to generate the initial anion-radical but also with other anions. So, the products of substitution may be obtained also with anions which do not enter into a common reaction with a substrate or react with it slowly. In other words, the catalytic amounts of a reactive nucleophile may induce the reaction and hence extend the limits of its application.[180] Sodium azide and α,*p*-dinitrocumene do not react with one another unless subjected to the action of light (48 hr). In contrast to sodium azide, the lithium salt of 2-nitropropane reacting with α,*p*-dinitrocumene in the dark gives following 3 hr the products of α-substitution in an 87% yield. When α,*p*-dinitrocumene (1 mol) is treated with sodium azide (2 mols) in the presence of the lithium salt of 2-nitropropane (0.1 mol), the initial α,*p*-dinitrocumene converts during 3 hr into *p*-nitrocumyl azide. The product is extremely pure, the yield is almost quantitative, and the reaction requires no UV-irradiation. The analogous pushing of the reaction was also observed for the pair *p*-nitrocumyl chloride–sodium nitrite. Typical one-electron donors, say, sodium naphthalenide, are used advantageously as pushing agents.[180]

Zoltewicz and Oestreich[181] used sodium methylate to accelerate and increase the yield of the reaction of 4-bromoisoquinoline and sodium thiophenolate. The ion CH_3O^- acts in this case as a competing electron-donor with respect to the ion PhS . However, if thiophenolate upon electron transfer to the substrate converts into the phenylthiyl radical and then to disulphide and is thus removed from the reaction sphere, the anion-radicals of the substrate generate in the presence of the methylate ion preserving a greater part of thiophenolate. The net rate of thioarylation in the presence of sodium methylate increases and the yield of 4-phenylthioisoquinoline rises. Azobenzene inhibits the action of sodium methylate. Scheme 56 summarizes what has been said above.

It is important to note that sodium methylate initiates only the formation of 4-phenylthioisoquinoline and the product of the competing substitution, 4-methoxyisoquinoline, is produced only in traces. The methylate ion, however, converts a part of the isoquinoline σ-radicals into the unsubstituted isoquinoline and produces formaldehyde.



Scheme 57.

Kornblum and Widmer[182] discuss ways of direct conversion of nitro compounds into thiols. Nitro compounds in DMSO are treated with a mixture of sodium sulphide and sulphur and then are reduced with aluminium amalgam (Scheme 57).

The first stage of the synthesis involves the interaction of a nitro compound with sodium sulphide. Sodium sulphide when used alone is only slightly effective: the reaction proceeds slowly and the yield is small. When elemental sulphur is added, the conversion markedly accelerates and the yield increases to 75–80%. The initiating effect of elemental sulphur can be easily explained if this is a radical-chain reaction. The reaction starts with one-electron transfer from the nucleophile to the nitro compound; further conversions are typical of mechanism $S_{RN}1$ (Scheme 58).

$$R_3C{-}NO_2 + {}^-S{-}S_X^- \longrightarrow R_3C{-}NO_2^{\cdot-} + {}^{\cdot}S{-}S_X^-$$

$$R_3C{-}NO_2^{\cdot-} \longrightarrow R_3C^{\cdot} + NO_2^-$$

$$R_3C^{\cdot} + {}^-S{-}S_X^- \longrightarrow R_3C{-}\dot{S}{-}S_X^-$$

$$R_3C{-}\dot{S}{-}S_X^- + R_3C{-}NO_2 \longrightarrow$$

$$\longrightarrow R_3C{-}NO_2^{\cdot-} + R_3C{-}S{-}S_X^-$$

$$R_3C{-}S{-}S_X^- \xrightarrow{Al/Hg} R_3C{-}S^- + S_X$$

Scheme 58.

It may be assumed that the donor activity of the nucleophile—sulphide ion—enhances as the negative charge is dispersed along the polysulphide chain in the ion produced from the sulphide upon the addition of elemental sulphur. This increases the mobility of electrons and facilitates electron transfer. Therefore this reaction may be initiated in such a simple way as the addition of elemental sulphur.

The interaction of a nitro compound with a nucleophile may be directed via a quite different route, that is the substitution of hydrogen for the nitro group. Kornblum *et al.*[183] used the methylthiolate ion as a sulphur-containing nucleophile. The first stages of the reaction are the same as described above; they generate the anion-radical of the initial nitro compound, which cleaves the nitro group to give the carbo-radical (Scheme 59). The latter captures hydrogen from methylthiolate and yields the product of denitration as illustrated in Scheme 59. Carbo-radicals carrying aryl substituents at α- and β-positions stabilize considerably at the expense of conjugation[183] and are less active hydrogen-acceptors than the carbo-radicals devoid of such substituents. The radicals carrying aryl substituents interacting with the methylthiolate ion give not only the products of denitration but also the anion-radicals of the corresponding methylthioester. Spin density in the aromatic nucleus of these aryl-containing anion-

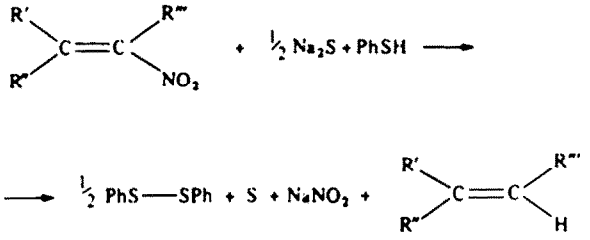
$$R_3CNO_2 + CH_3S^- \longrightarrow R_3CNO_2^{\cdot-} + CH_3S^{\cdot}$$

$$R_3CNO_2^{\cdot-} \longrightarrow R_3C^{\cdot} + NO_2^-$$

$$R_3C^{\cdot} + H_3CS^- \longrightarrow R_3C{-}H + H_3\dot{C}S^-$$

$$H_3\dot{C}S^- + R_3CNO_2 \longrightarrow H_3C{=}S + R_3CNO_2^{\cdot-}$$

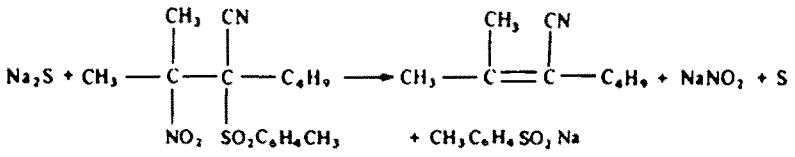
Scheme 59.



Scheme 60.

radicals delocalizes and this facilitates transfer of excess electron to the initial nitro compound or, in other words, promotes a chain process. As a result, the reaction with methylthiolate proceeds to a greater or lesser degree as the substitution of the nitro group by the thiomethyl fragment.[183] A distinguishing feature of Scheme 59 is that the anion-radical cleaves the nitrite ion as the leaving group. This peculiarity was used by Ono *et al.*[184] to prepare aryl-substituted olefins from nitroparaffins. Nitroparaffins while reacting with carbonyl compounds or aromatic imines may be converted into nitroarylolefins. Upon simple mixing with thiophenol and sodium sulphide in DMF, nitroarylolefins substitute hydrogen for the nitro group (Scheme 60). The authors[184] hold to the opinion that thiophenol adds to the olefin bond and an electron adds to the nitro group. Thus, the anion-radical $R'R''C(SPh)CH(R''')NO_2^{\cdot}$ controls the reaction. The final product is formed following cleavage of the nitrite ion and phenylthiyl radical (which gives diphenylsulphide). The yields of arylolefins are high and reach 80–95%.[184]

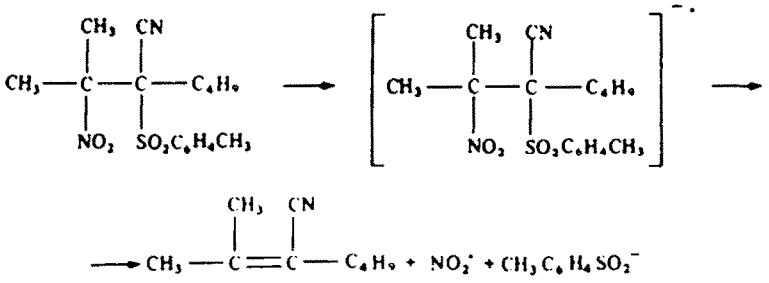
The production of olefins from β-nitrosulphones (Scheme 61) is as effective as the previous method; the reaction is conducted in DMF and requires no irradiation. The olefin forms in 97% yield (GLC data), but when separated, the yield in terms of pure substance is 70%.[185] The sodium salt of thiophenol may be used instead of sodium sulphide. Reaction 61 is of interest because it reveals an unusual effect of inhibitors.



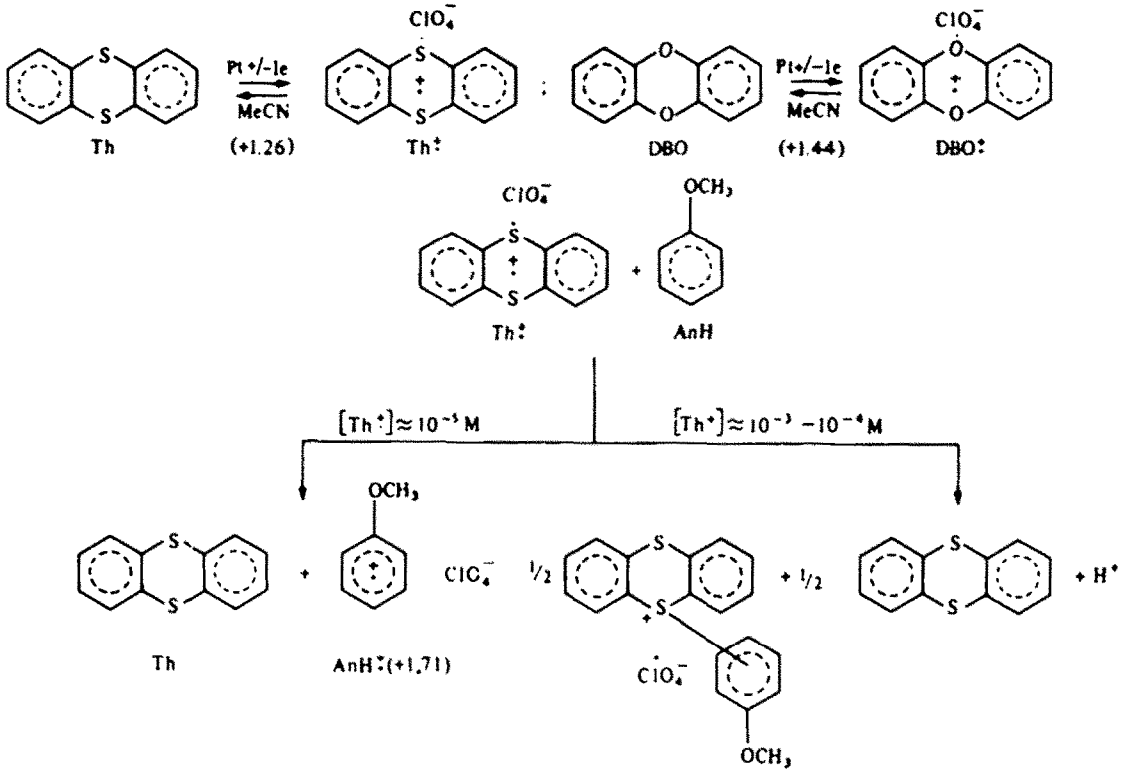
Scheme 61.

The reaction is ion-radical, as is demonstrated in Scheme 62. The authors[185] attribute the formation of olefin to the cleavage of the sulphinate ion and nitrogen dioxide. Small amounts of di-t-butylnitroxyl (5 mol%) completely inhibit the production of olefin. This points to a chain free-radical mechanism of the process. Aromatic nitro compounds which remove electrons from the anion-radical participating in the reaction usually inhibit ion-radical conversions. In the case of the conversions in Scheme 62, nitrobenzene, *m*- and *p*-dinitrobenzene (in amounts not exceeding 10 mol %) markedly accelerate the reaction.

Three acceptor groups in the molecule probably hold an unpaired electron on the anion-radical and prevent cleavage of the leaving group carrying this electron. Aromatic nitro compounds produce a donor–acceptor complex with the substrate anion-radical. The unpaired electron shifts to a π-acid



Scheme 62.



Scheme 63.

(nitro compound). This increases electron mobility and catalyzes elimination of leaving groups. Hence, in ion-radical reactions, inhibitors may become promoters, which should always be taken into account when developing ways of initiation of these conversions.

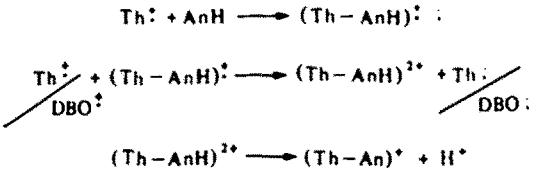
The reactions discussed so far involved anion-radicals. We now want to turn to the conversions of the cation-radical type. Scheme 63 visualizes the anisylation of the thianthrene cation-radical.[186]

The reaction gives the sulphonium salt (anion ClO_4) in a 90% yield. One-electron reduction of the thianthrene cation-radical by anisole is the side reaction. The dibenzodioxane cation-radical accelerates the reaction 200 times. This cation-radical is much more difficult to obtain than the thianthrenyl radical and therefore it is more active as an oxidizer.

When the concentration of the initial thianthrenyl radical drops from 10^{-3}–10^{-4} M to 10^{-5} M, the reaction takes another route: the sulphonium salt is not produced at all and one-electron transfer yields the uncharged thianthrene and the cation-radical of anisole (Scheme 63). Kinetic studies[186] have established that the anisylation of the thianthrenyl radical involves the following stages (Scheme 64):

(i) the formation of the thianthrene cation-radical complex with anisole; (ii) the oxidation of the cation-radical complex into the dicationic complex; this is the key stage of the process and it determines the rate of the reaction; (iii) rapid deprotonation of the dicationic complex yielding the final product—sulphonium salt.

Because a dicationic complex, $[Th\ AnH]^{2+}$, controls the reaction, the final result of the reaction should depend on the stationary concentration of this complex. From this the ways of regulating the process can be inferred: (iv) to increase the stationary concentration of complex $[Th\text{–}AnH]^{2+}$ a



Scheme 64.

$$PhSCH_3 \xrightarrow[-e]{} PhSCH_3^{\cdot+} \xrightarrow[-e,\,-H^+]{R(R')CHOH} Ph(CH_3)\overset{+}{S}-O-CH(R')R \xrightarrow[-PyH^+]{+Py}$$

$$\xrightarrow{+Py} PhSCH_3 + R(R')C{=}O$$

Scheme 65.

stronger oxidizer, as compared to the cation-radical of thianthrene, should be introduced into the reaction. This is the cation-radical of dibenzodioxane. It increases the rate of the reaction by two orders of magnitude: (v) to decrease the stationary concentration of complex $[Th\text{–}AnH]^{2+}$, it will suffice to lower the concentration of the oxidizer (it is the substrate), the thianthrene cation-radical. This also decreases the equilibrium concentration of the cation-radical complex $[Th\text{–}AnH]^{+\cdot}$. The rate of anisylation—the main process—sharply drops. The side process, one-electron transfer from anisole to the cation-radical of thianthrene, also decelerates but not so markedly. So, this side process remains the only one.

Shono *et al.*[187] recommend the use of thioanisole as a catalyzer—carrier—to lower the electrode potential in the oxidation of the secondary alcohols into ketones. The cation-radical of thioanisole is generated at a potential of up to +1.5 V (the background electrolyte is tetraethylammonium *p*-toluene sulphonate) in acetonitrile containing a pyridine base (Py) and a substrate. The yield of ketones depends on the alcohol nature and is 70–100%. The process takes place as shown in Scheme 65.

The process regenerates thioanisole and therefore a ratio of $R(R')CHOH : PhSCH_3 = 1:0.2$ is sufficient.

Let us now turn to the role that oxygen plays in ion-radical conversions. Oxygen is the main component of the air and, hence, is a typically active component of the medium in which chemical conversions mainly proceed.

Cation-radicals are often unstable and, therefore, they easily dissociate. If the dissociation is an equilibrium process, oxygen promotes it because it reacts with fragment ions produced in the decomposition. Therefore scientists prefer to conduct cation-radical processes in inert atmosphere, although oxygen (air) is, strictly speaking, inert with respect to primary cation-radicals. Exceptions to this rule are only those reactions where oxygen is required to obtain the cation-radicals from neutral molecules.

For anion-radicals, both oxygen and air (that is oxygen and carbon dioxide) are active components of the medium and so they should be removed prior to conducting reactions.

As a rule, air inhibits anion-radical reactions: a part of anion-radicals yields carboxylate and the other part gives an unpaired electron to oxygen thus converting anion-radicals into neutral molecules. Oxygen converts into the superoxide ion. This takes place if the acceptor organic molecule possesses a lower affinity for electron than oxygen or if one-electron oxidation of the anion-radical by oxygen proceeds more rapidly than its decomposition into a radical and anion.

If the oxidation is a slower process than the decomposition, oxygen may affect the nature of reaction products. Thus, treating *p*-nitrocumyl chloride with sodium malonate ester in a flow of pure dry nitrogen yields a product of C-alkylation.[188] The product has a structure analogous to the malonyl derivative of dicyanobenzene (Scheme 48); the yield is 90%. Oxygen completely inhibits the C-alkylation, and the reaction gives *p*-nitrocumyl alcohol in the same yield. When the malonate ion is lacking, oxygen is incapable of converting *p*-nitrocumyl chloride into the alcohol.[188] In the presence of oxygen the reaction develops in two directions with different speeds. The reaction first produces anion-radicals of *p*-nitrocumyl chloride (the source of electrons is the malonate anion) and, then, chloride ions cleave from these anion-radicals. Nitrocumyl radicals accumulate at a faster rate than the initial anion-radicals perish under the effect of oxygen. Therefore oxygen may trap only cumyl radicals and give radicals of cumylperoxide which convert into the hydroperoxide when adding hydrogen of the solvent. The hydroperoxide decomposes and forms cumyl alcohol. The conversion is highly selective since the yield of the latter product reaches 90%.

Let us now turn to a case where the accepting ability of oxygen is lower than that of a substrate but greater than that of charged intermediate or final products of anion-radical conversions. The superoxide ion is produced at the final stages of the process and acts as an electron carrier with respect to the substrate, thus branching the chain process. In other words, oxygen promotes rather than inhibits these reactions. This conclusion is especially important for practical organic synthesis. As has

been reported,[189] the reaction between 1-nitroanthraquinone and sodium methylate in DMSO–methanol (7 : 1) accelerates when conducted in air and not under argon. In the absence of air, anion-radicals of 1-nitroanthraquinone obtained in DMSO electrolytically, do not change upon the addition of MeOH or NaOMe.[189] When air gains access to the system, the anion-radicals are consumed completely and produce 1-methoxyanthraquinone (the main product) and 1-oxyanthraquinone (the admixture). Oxygen, therefore, promotes methoxylation by the anion-radical mechanism. An earlier study has revealed that methoxylation of 2,4-dinitrochlorobenzene accelerates by an order of magnitude when conducted in air rather than under nitrogen.[190] The authors[190] proposed the scheme according to which no initial substrate undergoes methoxylation but rather its anion-radical. This produces the radical anion σ-complex which is oxidized by oxygen into the anionidic σ-complex carrying no unpaired electron. This stage generates the superoxide ion which later advantageously competes with the methoxide ion in one-electron reduction of the initial 2,4-dinitrochlorobenzene. The main point with respect to the catalytic effect of oxygen is the ability of the superoxide ion to transfer electron to strongly accepting molecules of the substrate. This was confirmed by electrochemical generation of peroxide ions: *o*- and *p*-nitrochlorobenzenes and *o*-nitrobromobenzene react with these ions in DMF giving *o*- and *p*-nitrophenols.[191] Frimer and Rosenthal[192] treating 2,4-dinitrobromobenzene with $K^{18}O_2$ in the presence of dicyclohexyl-18-crown-6-ether (the solvent is benzene saturated with ^{16}O) obtained 2,4-dinitrophenol carrying practically no ^{18}O. According to mass-spectrometric data,[192] the content of the label in phenol was below 10%. Hence, superoxide ion $^{18}O_2^{\cdot-}$ only transfers electron to the substrate, and phenol is produced as a result of the reaction between the anion-radical of 2,4-dinitrobromobenzene or 2,4-dinitrophenyl radical and ^{16}O.

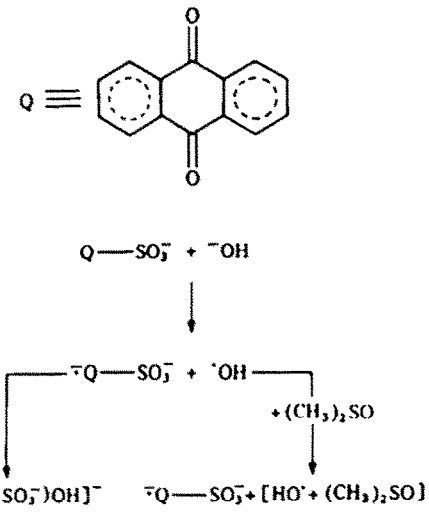
It should be noted in conclusion that a tradition to conduct ion-radical conversions in inert atmosphere may sometimes end in failure. Oxygen accelerates the reactions involving strongly accepting substrates. This is similar to a promoting effect of active organic oxidizers of the dinitrobenzene type.

6. *Effect of solvents*

Ion-radical reactions proceed easier the less the number of factors decreasing the stability of ion-radicals. Since the latter are charged particles carrying an unpaired electron, the solvent should also be polar, incapable of splitting, cleavage of cationic or anionic groups and also cleavage of the radical particles of the hydrogen atom type.[193] This is of course a general characteristic which has as many peculiarities as is the number of solvents. These peculiarities, however, may be analyzed with respect to their effect on ion-radical conversions. This will be illustrated on the example of a solvent most commonly used in ion-radical reactions, that is dimethylsulphoxide. It plays different roles in different reactions. In reaction 55 it increases the stability of the intermediate radical particle saving it for the attack of the phenylthiolate ion. Dimethylsulphoxide, however, may completely inhibit the substitution, as has been reported by Fomin *et al.*[194] for hydroxylation of anthraquinone sulphoacids (Scheme 66). The hydroxylation starts only at elevated temperatures and proceeds at a high rate at 180–200°. The authors[195] adduce arguments in support of the hidden-radical mechanism of the reaction when the main part of the quinone anion-radicals do not pass into the solvent pool (Scheme 66). The hydroxylation of a greater part of the substrate molecules proceeds by the pathway not involving the passage of intermediate particles into the volume. The final products are oxyanthraquinones. When the reaction is conducted in DMSO, $OH^{\cdot}$ radicals form complexes with the solvent molecules, and the process is directed via the route involving the passage of the sulphoanthraquinone anion-radicals into the solvent pool. This facilitates the first stage; anion-radicals of the initial anthraquinone sulphoacid are produced already at 25° and their accumulation is completed in several hours.[196] The reaction, however, does not proceed further and hydroxyl does not replace the sulpho group: hydroxyl radicals irreversibly combine with DMSO, and methyl radicals are liberated (Scheme 66). The production of free radicals $CH_3^{\cdot}$ from DMSO was proved by independent experiments.[197]

Thus, dimethylsulphoxide in reaction 66 behaves as an active medium preventing the development of the ion-radical process. In some reactions, however, it promotes the ion-radical conversion. This is, for instance, a common method of conversion of tertiary aliphatic nitro compounds into nitromethyl derivatives and further into aldehydes[198] (Scheme 67).

To prepare the reagent $Na^+ \ CH_2NO_2$, sodium hydride is reacted with nitromethane in the same solution which is used later to replace the nitro group by fragment CH_2NO_2 (see Scheme 67). The

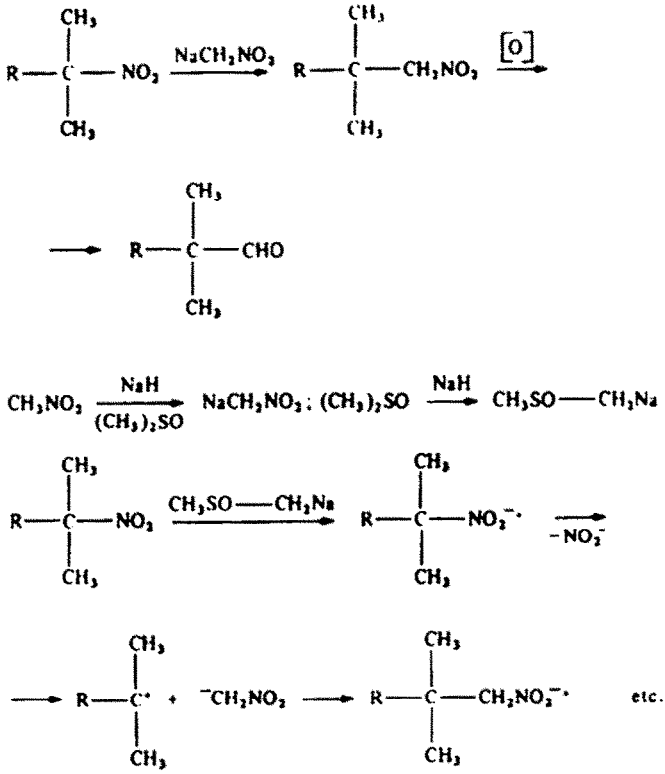


Scheme 66.

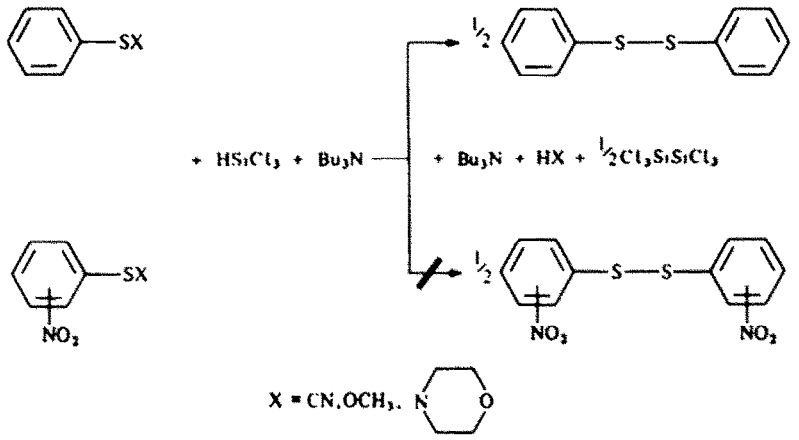
reaction proceeds most effectively in DMSO. Kornblum and Erickson[198] attribute this to small amounts of sodium dimsyl produced in DMSO. It acts as a powerful one-electron reducer inducing (entraining) the chain anion-radical process as has been discussed above. When conducted in DMF instead of DMSO the reaction decelerates.[198]

7. *Directed effect*

Oxidation-reduction interaction between components of the ion-radical salt. This interaction is of particular interest because it is directly connected to the problem of removing the nitrosulphenate protection. The nitroarylsulphenate protection is used in different conversions of complex, in particular, bioorganic, molecules carrying amino and oxy groups. To restore the activity of amino or



Scheme 67.



Scheme 68.

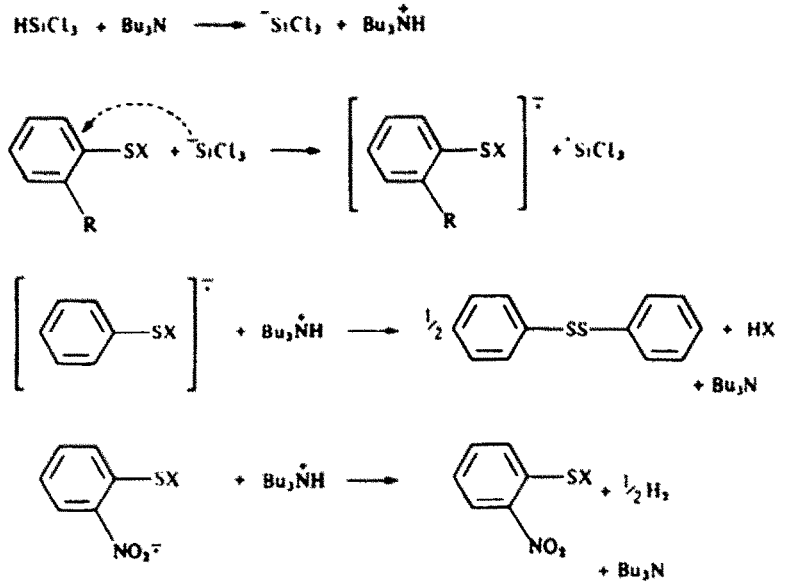
oxy groups in the final product, the protection should be removed. To this end, the competition of acceptor fragments should be taken into account; otherwise it would be the nitro group rather than the sulphur-containing group that is reduced. The trichlorosilane–butylamine system has been studied along with a number of reducing systems.[199,200] As has been revealed, trichlorosilane and tributylamine reduce only arylsulphene derivatives not carrying the nitro group. Nitroarylsulphenate analogues do not change under these conditions (Scheme 68).

Nitrosulphene derivatives introduced into the mixture of trichorosilane and tributylamine liberate hydrogen. Mixing only trichlorosilane and tributylamine (not adding the nitroarylsulphenate component) does not produce hydrogen.

Trichlorosilane and tributylamine yield the trichlorosilyl anion and the tributylammonium cation. This stage starts a series of conversions involving one-electron transfer from the trichlorosilyl anion to the sulphene molecule. Benzenesulphene derivatives produce anion-radicals which are unstable and immediately convert into disulphides. Nitrobenzenesulphenic compounds form stable anion-radicals which give up an electron to the proton of the counter-ion, i.e. tributylammonium cation (Scheme 69).

The anion-radical carrying a nitro group undergoes one-electron oxidation by a proton, and this liberates hydrogen, rather than cleaves the sulphur-containing fragment.

Benzene sulpheneamides or benzene rhodanides react with the trichlorosilyl anion in the same way as benzenesulphene esters: only the analogues carrying no nitro group are reduced, whereas the nitrated derivatives remain unchanged.[200] By contrast, nitrobenzenesulphene chlorides reduce in the



Scheme 69.

Table 4. Effective charges on groups R and SX in ion-radicals of type $RC_6H_4SX^{\cdot-}$

Groups		Charges on groups	
R	SX	R	SX
H	SCl	—	−0.78
NO_2	SCl	−0.20	−0.76
H	SCN		−0.54
NO_2	SCN	0.48	−0.27

system Bu_3N–$HSiCl_3$ as advantageously as benzenesulphene chloride itself.[200] This peculiarity of group S—Cl is not self-evident because the polarization of S—CN and S—Cl bonds is comparable. To illustrate[201] both nitroaryl rhodanides and nitroarylsulphene chlorides when dissolved in a concentrated sulphuric acid produce arylsulphenium ions ArS^+. It may be thought that in the anion-radical state of the molecule, groups SCN and SCl should differ in the liability to localize an unpaired electron at least in the presence of a conjugated nitro group. Authors[202] conducted quantum-chemical INDO/2 calculations of anion-radicals $C_6H_4SCl^{\cdot-}$, $C_6H_5SCN^{\cdot-}$, $O_2NC_6H_4SCl^{\cdot-}$, $O_2NC_6H_4SCN^{\cdot-}$, the results of calculations give a clear-cut explanation of the established difference (see Table 4).

The table shows that for anion-radicals of the sulphene chloride series, the charge on group SCl is only slightly dependent on the presence or absence of the nitro group in the aromatic nucleus. For anion-radicals of the rhodanide series, the nitro group present in the molecule reduces the charge on SCN twofold. In other words, while competing for an unpaired electron in the anion-radical, group SCl should be stronger and group SCN weaker than group NO_2.

As follows from the above, a change in the distribution of an unpaired electron under the effect of the nitro group is decisive for reactions starting with the production of anion-radicals. The nitro group traps an unpaired electron thus protecting SOR, SNR_2 and SCN groups from reductive cleavage.†

In a similar way, the direction of reducing cleavage of aryltetrasolium esters, ArOTz, depends on the localization of spin density in the intermediate anion-radical. When the electron is localized in the Tz nucleus, the esters cleave by the scheme:

$$Tz\text{–}OAr^{\cdot-} \rightarrow Tz^{\cdot} + ArO^-.$$

When the Ar nucleus demonstrates the highest spin density as, say, in anion-radical 5-(*p*-cyanophenoxy)-1-phenyltetrasole, the cleavage proceeds by the following scheme:[203]

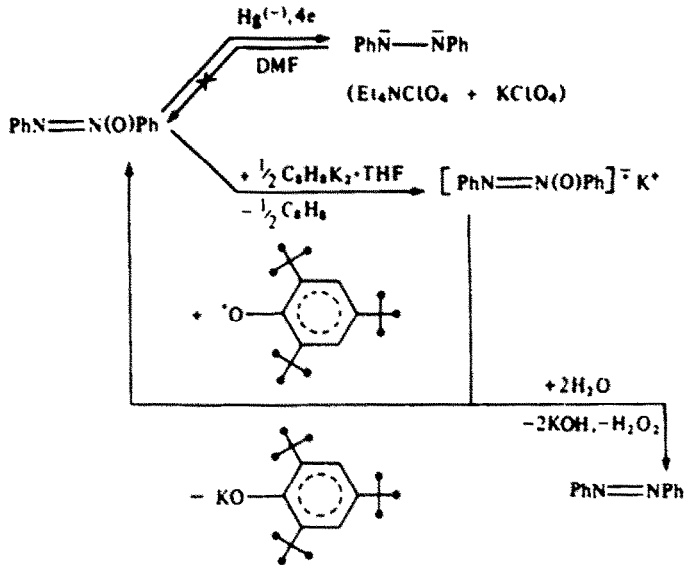
$$TzO\text{–}Ar^{\cdot-} \rightarrow TzO^- + Ar^{\cdot}.$$

Coordination interactions in a salt-like product of electron transfer. Let us analyze transfer of electrons to two simple organic substances: azoxybenzene and 2,5-dirhodanothiophene.

Multielectron reduction of azoxybenzene on a dropping mercury electrode gives an azodianion (Scheme 70). In the absence of protons a polarogram shows a wave corresponding to transfer of four electrons for each molecule of azoxybenzene. The nature of cation (tetraalkylammonium, potassium) does not change the pattern of reduction.[204] In the liquid phase, however, when dipotassium cyclooctatetraene acts as a "dissolved electrode", the reduction of azoxybenzene stops at the very first stage, that is after transfer of one electron.[205–207] This produces the azoxybenzene anion-radicals which do not reduce further despite the presence of electron donors in the solution (Scheme 70). The ESR method practically does not reveal these anion-radicals although one-electron oxidation by the phenoxyl radical quantitatively generates azoxybenzene and produces the corresponding potassium phenolate in a quantitative yield. Treatment with water gives azobenzene in a 100% yield (Scheme 70).

The authors[205–207] explain this as follows. In a liquid phase, primary anion-radicals of azoxybenzene stabilize due to their bonding to potassium cations. This yields the coordination

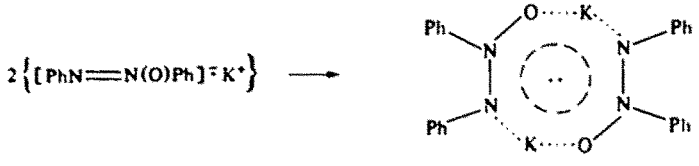
† What is important for practical organic synthesis is that the liability of groups SOR and SNR_2 to undergo the reductive cleavage markedly increases after their preliminary protonation. In the trifluoroacetic acid–triethylsilane system, the reduction proceeds completely selectively, strictly at the expense of the sulphur-containing group. The products are formed in quantitative yields. The nitro group does not inhibit the reaction.[199,200]



Scheme 70.

complex (see Scheme 71); the complex is diamagnetic and, therefore, the azoxybenzene anion-radicals cannot be revealed by ESR spectroscopy.

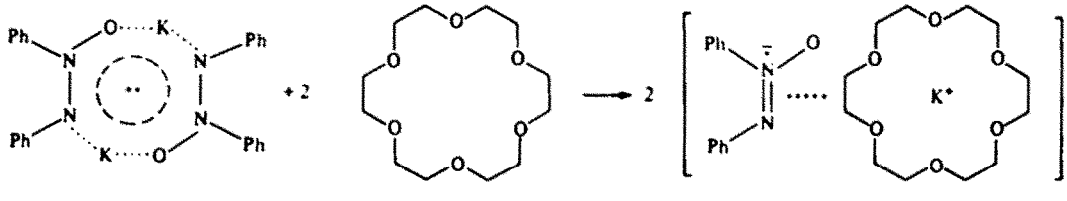
The dimeric complex illustrated in Scheme 71 is not liable to further reduction by dipotassium cyclooctatetraene, which saves the anion-radicals from converting into azodianions. Potassium cations play an important role in such a limitation of reduction (which, as a rule, proceeds easily, see electrode reaction 70). When potassium cations leave the sphere of reaction by combining with 18-crown-6-ether according to Scheme 72, the liquid-phase and the electrode reduction proceed in a similar manner. The liquid-phase process in the presence of crown ether also generates an azodianion



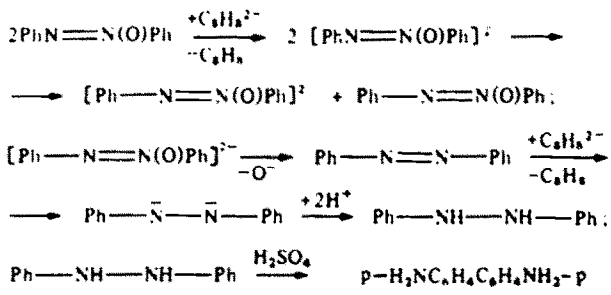
Scheme 71.

identified through benzidine after protonation and rearrangement.[206] Scheme 73 visualizes liquid-phase conversions of azoxybenzene which take place under the effect of dipotassium cyclooctatetraene in the presence of crown ether.

Based on anion-radical conversions of azoxybenzene, the directed "matrix" synthesis of cyclic poly-(thienylene-2,5-disulphide) from 2,5-dirhodanthiophene was carried out (Scheme 74). The 2,5-dirhodanothiophene anion-radical is unstable and immediately converts into the 2-rhodanothiophene-5-thiyl radical transferring one more electron. So, one of the rhodanide groups may be reduced to a mercaptide group and the latter may interact with the residual rhodanide group.



Scheme 72.



Scheme 73.

As it was suggested, the sulphur of the thiophene nucleus is liable to coordinate with the potassium cation in the formation of disulphide:

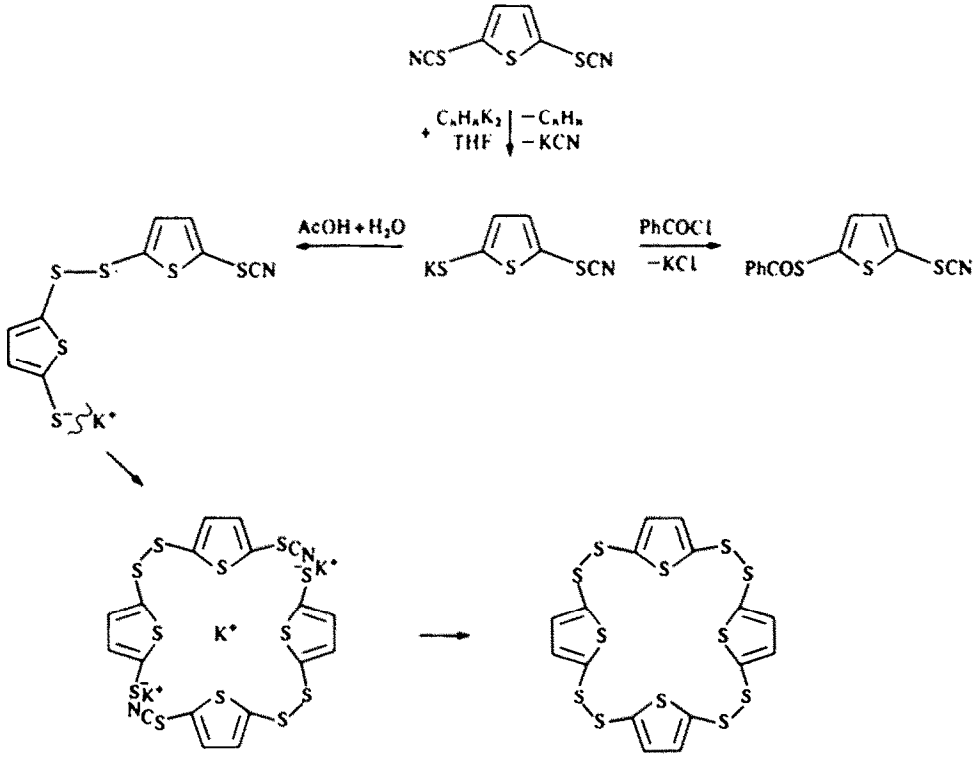
$$(-S\ )+(NSC\ )\rightarrow(-S-S-)+CN^-.$$

This gave grounds to believe that anionic fragments may be "assembled" in a matrix form to yield a cyclic product. Reacting equimolar amounts of 2,5-dirhodanthiophene and dipotassium cyclooctatetraene in THF produces 5-rhodano-2-thienylmercaptide of potassium, potassium cyanide and cyclooctatetraene. Potassium rhodanothienylmercaptide is stable in THF and was characterized through a monobenzoyl derivative.[208] The addition of water to THF produces polydisulphide. X-ray analysis has unambiguously established that polydisulphide has a cyclic structure.[209] The cyclisation most probably proceeds through intermediate disulphides by Scheme 74.

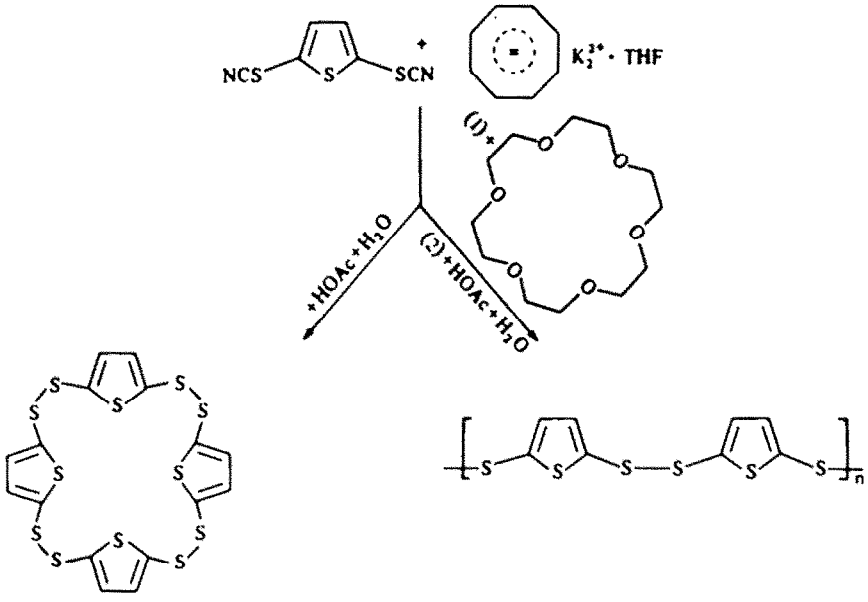
In the homogeneous reduction, the metal cation coordinates anionidic fragments and enables their bonding within the matrix. The comparison of the diameter of the obtained multithiaheterocycle cavity with a doubled radius of the potassium cation agrees with this mechanism.

In the electrode reduction conducted in the same solvent (THF), both rhodanide groups in 2,5-dirhodanothiophene cleave immediately within one four-electron wave.[207]

The homogeneous and electrode reactions may yield approximately the same results when 2,5-dirhodanothiophene reacts with dipotassium cyclooctatetraene in the presence of crown-18-ether-6.



Scheme 74.



Scheme 75.

This ether combines the potassium cation and directs the condensation towards formation of linear rather than cyclic product (Scheme 75).

Schemes 71, 73 and 75 demonstrate that coordination to the metal cation decisively changes the direction of further conversion of electron-transfer products.

IV. CONCLUSION

The analysis of different ways of identification of ion-radical reactions has yielded the following results.

1. None of the approaches can, by themselves, identify an ion-radical conversion.
2. A set of suitable methods gives reliable information on the role the ion-radical stage plays in the net mechanism of reaction.
3. A choice between the standard and the ion-radical mechanism of reactions is quite an important problem, especially in cases when ion-radicals leave the solvent cage or direct the reaction via another pathway yielding products of peculiar structure, making the conversion conditions more mild, and changing the reactivity of secondary intermediate particles. If ion-radicals form and react in the solvent cage, and the reaction proceeds rapidly, or if it yields products indistinguishable from "standard" products, the role the ion-radicals play is only of theoretical interest and is so far not essential for practical organic synthesis.
4. The ion-radical mechanism should be checked with respect to every particular reaction. Compounds of even one class may behave differently : some of them react by the ion-radical mechanism while the others may take quite another pathway. Besides, the notion of one-electron transfer cannot be applied to absolutely all cases without exception.
5. The results yielded by different methods should agree. Only such an approach may reveal the real mechanism of reaction. These general estimates have been already reported by us[210] and they were confirmed by later experiments.

Methods of initiation of ion-radical conversions depend on the nature of reacting particles which possess ionic and radical properties. Since these particles are charged they require special solvents, interact with counter-ions and react with particles of the opposite charge. The presence of an unpaired electron makes ion-radicals sensitive to magnetic effects and sometimes to irradiation and especially sensitive to structural factors affecting the intramolecular distribution of spin density. The ionic and radical properties of molecules determine a wide range of methods to inhibit the undesirable processes and to entrain the reactions giving the necessary end products. Ion-radical particles, however, are less

stable than ordinary ions or neutral molecules. As a rule, they exist only at reduced temperatures. Therefore, heating is not a typical way of promoting ion-radical conversions. These reactions are often conducted in an inert gaseous atmosphere, in apparatus having smooth walls, etc. It is the reactivity of ion-radicals that makes the control over the reactions taking the ion-radical course so precise.

The analysis of references to this review yields the following information. The publications on the subject double, on the average, during five years, that is half the usual time. The number of references on works mentioned in this review doubles, on the average, over a period of two and a half years. In other words, references accumulate twice as fast as the primary publications. The most productive authors are, as a rule, most often cited. Practically any communication devoted to the problem arouses considerable interest. Organic ion-radical reactions are studied in 25 countries. The U.S.A., U.S.S.R., Japan and Italy top the list of publications. Twenty per cent of all articles irrespective of the country where they have been carried out are published in the *Journal of the American Chemical Society*.

Thus, this field of research attracts widespread attention and receives a large development effort. The solution of one problem poses other problems and so patience in the research often has a greater value than inspiration.

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