Translated from *Uspekhi Khimii*, **57**, 254-280 (1988) U.D.C. 542.958.1 + 541.515

The Oxidation-reduction Stage in the Nitration Reaction

A.S.Morkovnik

The mechanism of the nitration of aromatic compounds in which the initial stage is the oxidation of the aromatic substrate to the radical-cation is examined. Certain general preconditions, which make such a mechanism feasible, and also the available experimental evidence for its operation are analysed.
The bibliography includes 219 references.

CONTENTS

I. Introduction 144
II. The formation of the radical-cations of aromatic compounds under nitration conditions and their conversion into nitro-compounds 144
III. Nitration of aromatic compounds by the nitronium cation 148
IV. Catalytic nitration 150
V. The change in the mode of reaction after a change in the reactant ratio 153
VI. Nitration of aromatic compounds by tetranitromethane and metal nitrates 154
VII. The radical-ion mechanism of the nitramine rearrangement and the isomerisation of nitroarenium cations 155

I. INTRODUCTION

The reactions of organic compounds with electrophiles are known to begin with electron transfer from the substrate to the reactant and the formation of radical-cation (RC) of the organic compound:[1,2]

$$RH + E^{\cdot} \rightarrow RH^{+} + E^{-} \rightarrow \text{products}.$$

The oxidation-reduction stage in reactions of this type is frequently masked by the rapid subsequent reactions of the RC and the electrophile reduction product, which is a manifestation of the non-radical character of the overall process.[1,2] In such cases, the study of the reaction mechanism involves considerable experimental difficulties and its determination makes it necessary to resort to various indirect data apart from the investigation of the kinetics. These difficulties are a consequence of fundamental limitations characteristic of classical kinetics which make it impossible to obtain direct information about the fastest stages of chemical reactions. As a result, in the words of Hoffmann,[3] with the aid of kinetic studies it is possible to obtain "only the lower limit... to the number of stages in a reaction sequence and hence to the number of intermediate species".

The question of electron transfer as a possible elementary step in the reaction arises, in particular, in the study of the nitration of aromatic compounds. The energies of the highest occupied molecular orbitals (HOMO) of aromatic compounds are frequently close to or even exceed the energies of the lowest unoccupied molecular orbitals (LUMO) of the electrophiles involved in the nitration, which creates a possibility for an exoergic one-electron transfer in the direction from ArH to the electrophile in the case of activated aromatic substrates.

The experimental study of this problem, first formulated in the 1940's–1950's,[4-7] became possible only recently as a result of the advances achieved in the study of the RC of aromatic compounds ArH^{+}. Although the data obtained hitherto do not provide an exhaustive answer to the question of the role of the RC in nitration reactions, they nevertheless permit the conclusion that significant progress has been achieved in the solution of this problem. Some of these data are difficult to explain from the standpoint of classical ideas about the nitration mechanism[8] and are therefore of fundamental importance.

It is noteworthy that the problem of electron transfer as a possible stage in electrophilic substitution in aromatic compounds has already been frequently discussed.[9-16] However, it has not been the subject of a special detailed examination in relation to nitration. This factor and also the significant progress in the study of electron transfer processes in ArH–nitrating agent systems, which has occurred in recent years, made it desirable to write the present review devoted to the role of RC in nitration reactions.

II. THE FORMATION OF THE RADICAL-CATIONS OF AROMATIC COMPOUNDS UNDER NITRATION CONDITIONS AND THEIR CONVERSION INTO NITRO-COMPOUNDS

1. One-Electron Oxidation of Aromatic Compounds By Nitrating Agents

The oxidation reactions of aromatic compounds under the influence of nitrating agents are extremely varied and have long been known.[17] However, the possibility of the simplest of them, namely the one-electron oxidation of aromatic substrates in which the latter lose one π electron and are converted into highly active RC, has been demonstrated only recently:

$$ArH \xrightarrow[-e]{\text{nitrating agent}} ArH^{+}$$

The range of ArH capable of reacting in this way is fairly wide and according to the available data includes aromatic compounds with strong and moderate reducing properties, such as naphthalene,[18] sterically hindered phenols,[19] various aromatic amines,[20-23] and certain heterocyclic compounds.[20,21,24-27]

The formation of RC has been most often demonstrated by the usual spectroscopic methods. In a series of reactions of activated aromatic compounds with nitrating agents, RC were isolated preparatively in the form of salts with weakly nucleophilic anions[22,27-29] (Table 1). The formation of extremely unstable RC, such as, for example, the RC derived from toluene (its lifetime in 2 M $HClO_4$ solution is less than 3.3×10^{-7} s [30]) by these procedures is difficult or impossible. An indirect sign of the formation of such species is the presence

in the reaction product of biaryls (dehydrodimers), which usually arise on dimerisation of the RC: [20,31]

$$2ArH^{+\cdot} \rightarrow \overset{+}{A}r(H) - \overset{+}{A}r(H) \rightarrow Ar - Ar + 2H^+$$

An alternative reaction, which also leads to biaryls, involves the attack on the substrate by the arenium cation ArH_2^+ or $ArHNO_2^+$. [32–34]

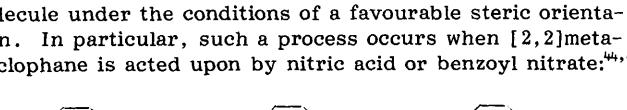
Table 1. The yield of radical-cations in reactions involving the one-electron oxidation of aromatic compounds by nitrating agents.

ArH	Nitrating agent	Solvent	W*, %	Method of determination	Refs.
Phenothiazine	HNO_3	CH_3CN	70	spectrophotometry	[20]
Phenothiazine	HNO_3	$HClO_4$	78	isolation of RC salt	[20]
N-Methylphenothiazine	HNO_3	$ClCH_2CH_2Cl$	35	stopped flow method	[21]
Phenoxazine	HNO_3	CH_3COOH	80	spectrophotometry	[20]
Dibenzo-*p*-dioxin	HNO_3	CF_3COOH	95	spectrophotometry	[25]
NN-Dimethyl-9,10-dihydrophenazine	HNO_3	$ClCH_2CH_2Cl$	97	spectrophotometry	[21]
NNN'N'-Tetramethyl-*p*-phenylenediamine	HNO_3	$ClCH_2CH_2Cl$	85	spectrophotometry	[21]
NNN'N'-Tetramethylbenzidine	HNO_3	CH_3CN	10	spectrophotometry	[20]
Tri-*p*-tolylamine	HNO_3	$ClCH_2CH_2Cl$	79	spectrophotometry	[21]
N-Methylcarbazole	HNO_3	$HClO_4$	95	from the yield of the biaryl RC	[40]
N-Methylcarbazole	HNO_3	CF_3COOH	24	from the yield of biaryl	[20]
1,3-Diphenyl-2-pyrazoline	HNO_3	$HClO_4$	97	from the yield of the biaryl dication	[40]
1,3,5-Triphenyl-2-pyrazoline	NO_2BF_4	CH_3CN	30	from the yield of biaryl	[23]
NN-Dimethylaniline	HNO_3	$HClO_4$	66	from the yield of the biaryl dication	[22]
NN-Dimethylaniline	NO_2BF_4	CH_3CN	12	from the yield of the biaryl dication	[23]
6-Methoxy-1,3-dimethyl-1,2-diaza-1*H*-phenalene	$NaNO_2$	CH_3COOH	75	isolation of the RC salt	[27]

*The yield of the RC estimated from the maximum observed concentration of the RC in the ArH–nitrating agent system or the preparative yield of the RC salt or biaryl. In the last case, the yield is quoted on the assumption that the biaryl is formed as a result of the dimerisation of the RC.

Biaryls are formed as side or main products in the nitration of alkylbenzenes, [35–37] diphenylene, [38] furan, [39] 9-methylcarbazole, [20,40] *NN*-dimethylaniline, [22,31,41] aminonaphthalenes, [42] and derivatives of 1-phenyl-2-pyrazoline [20,40] and 2-acetyl-1-phenylpyrazolidine. [43] It has been established that dehydrodimerisation of alkylbenzenes proceeds without the involvement of the protonated form of the hydrocarbons. [36]

The "cross linking" of the aromatic nuclei under nitration conditions occurs also when they are fragments of a single molecule under the conditions of a favourable steric orientation. In particular, such a process occurs when [2,2]metacyclophane is acted upon by nitric acid or benzoyl nitrate: [44,45]



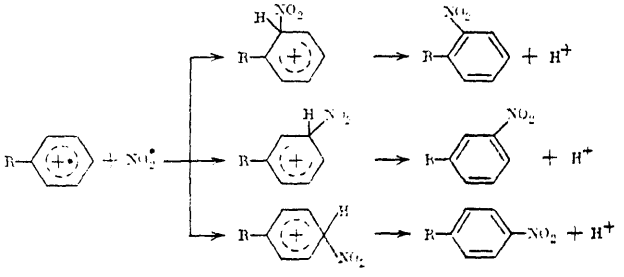
(I)

The initial stage in these reactions leads in all probability to the oxidation of compound (I) to the RC, since it is known [46–48] that the RC of [2,2]metacyclophanes are readily converted into tetrahydropyrenes. Analogous processes have been observed [49] also in the nitration of [3,2]metacyclophanes.

The one-electron oxidation of aromatic compounds by nitrating agents constitutes in many instances an independent reaction leading to the formation of RC as the final product, sometimes in a nearly quantitative yield [25,27,28,40] (Table 1).

2. The Conversion of the Radical-Cations of Aromatic Compounds into Nitro-Compounds

The RC are converted into nitro-derivatives when they are acted upon by nitrogen dioxide [formed in Ar–H–oxygen compounds of nitrogen(V) systems as a result of the reduction of the nitrating agent by the substrate] or the nitrite ion. In the latter case, the initial stage of the reaction is usually the one-electron reduction of the RC by the nucleophile: [50–52]



$$ArH^{+\cdot} + NO_2^- \rightarrow ArH + NO_2^{\cdot}$$

$$ArH^{+\cdot} + NO_2^{\cdot} \rightarrow ArNO_2 + H^+$$

$$2ArH + 3NO_2^{\cdot} \rightarrow 2ArNO_2 + NO^{\cdot} + H_2O$$

The recombination of the RC with $NO_2^{\cdot}$ should be regarded as a special case of little investigated reactions of the following type: [53–58]

$$ArH^{+\cdot} + R^{\cdot} \rightarrow ArHR^+ \rightarrow ArR + H^+$$

The RC dimerisation processes are related to these reactions. [50,59] The results of studies of the interaction of the RC with nitrogen dioxide, carried out mainly in recent years, will be examined below.

Initially an attempt was made to achieve the reactions of RC with nitrogen dioxide by subjecting aromatic compounds to one-electron oxidation (chemical or electrochemical) in the presence of $NO_2^{\cdot}$. The nitration of naphthalene [60] and mesitylene [61] observed under these conditions was interpreted as a result of the recombination of the RC of the hydrocarbons with nitrogen dioxide in accordance with the scheme

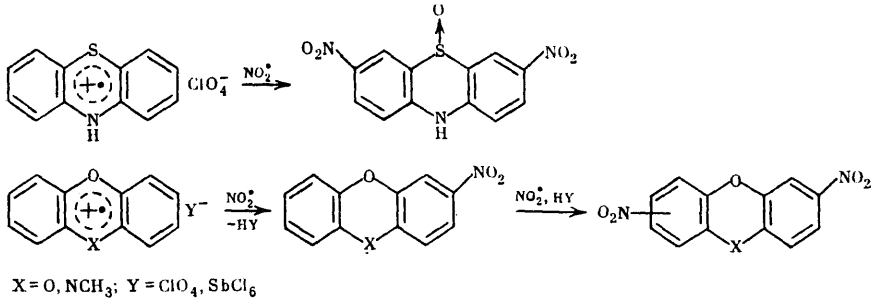
$$ArH \xrightarrow{[Ox]} ArH^{+\cdot}$$

$$ArH^{+\cdot} + NO_2^{\cdot} \rightarrow ArHNO_2^+ \rightarrow ArNO_2^{\cdot} + H^+$$

[Ox] = $Ce(NH_4)_2(NO_3)_6$, or the anode; ArH = naphthalene or mesitylene.

However, the quantitative oxidation of the initial compounds to the RC was not ensured under these conditions, since the hydrocarbons reacted too slowly with the one-electron oxidants. [62] They underwent much faster direct nitration by nitrogen dioxide, which is catalysed by the strong acids accumulating in the ArH–$NO_2^{\cdot}$–[Ox] system. This process has in fact been the source of nitroarenes (at least of the bulk of the latter). [62] Thus the data quoted above [60,61] neither confirmed nor disproved the possibility of the recombination of the RC with nitrogen dioxide.

Unambiguous evidence for the ability of the RC to react with $NO_2^{\cdot}$ was obtained using stable RC. [22,25,51,63,64] It was found that even RC with a comparatively low reactivity are capable of reacting with $NO_2^{\cdot}$ to form nitro-compounds. The objects of studies were the perchlorates of the RD derived from phenothiazine, [63] *N*-methylphenoxazine, [22] the hexachloroantimonate of the RC obtained from dibenzo-*p*-dioxin, [25] and the hexafluorophosphates of the dimeric RC derived from naphthalene, [51] mono- and di-methylnaphthalenes, [64] pyrene, [64] and perylene. [52] In the case of the first three RC (the reactions were carried out in acetonitrile), nitro-products corresponding to attack on the RC at positions with the maximum unpaired electron density were obtained: [25,65]



X = O, NCH_3; Y = ClO_4, $SbCl_6$

The direct nitration of the corresponding heterocyclic compounds leads to analogous results.[22,25,63]

Table 2. The selectivity of the direct nitration of hydrocarbons of the naphthalene series (ArH) and of the recombination of the corresponding dimeric RC of the type $(ArH)_2^+$ with nitrogen dioxide.[64]

ArH	Nitration conditions	Yields of products of mononitration of ArH in individual positions, %					Distribution of spin density in RC
		1	2	4	5	8	
Naphthalene	A	97—98	2—3	—	—	—	C (1) > C (2)
	E	91	9	—	—	—	
1-Methylnaphthalene	A	—	8	88	1	3	C (4) > C (5) >
	B	—	18	66	10	6	> C (8) > C (2)
	C	—	31	56	8	5	
2-Methylnaphthalene	A	84	—	10	3	3	C (1) > C (8) >
	B	65	—	17	7	9	> C (4) > C (5)
	C	56	—	16	11	12	
1,4-Dimethylnaphthalene	A	—	95	—	5	—	C (5) > C (2) > C (6)
	B	—	3	—	5	—	
	C	—	6	—	18	—	
1,8-Dimethylnaphthalene	A	—	8	92	—	—	C (4) > C (2) > C (3)
	B	—	12	88	—	—	
	C	—	70	30	—	—	
	D	—	21	79	—	—	
2,3-Dimethylnaphthalene	A	90	—	—	10	—	C (1) > C (5) > C (6)
	B	77	—	—	21	—	
	C	77	—	—	18	—	
2,6-Dimethylnaphthalene	A	90	—	10	—	—	C (1) > C (4) > C (3)
	B	78	—	22	—	—	
	C	84	—	15	—	—	

Note. A) An excess of the RC salt was treated with nitrogen dioxide in CH_2Cl_2 at −70—−20 °C; B) nitration of ArH with nitrogen tetroxide in CH_2Cl_2 at 20 °C; C) nitration of ArH with acetyl nitrate in acetic anhydride at −30 °C; D) nitration of ArH with nitric acid in acetic acid at 25 °C; E) nitration with nitronium tetrafluoroborate in CH_2Cl_2 at 25 °C.

The dimeric RC obtained from hydrocarbons of the naphthalene series recombine with $NO_2^\bullet$ to form mixtures of mononitro-derivatives, which have the same qualitative composition as the products of the direct nitration of the corresponding hydrocarbons,[64] for example:

$$(C_{10}H_8)_2^{\bullet+}\,PF_6^- + NO_2^\bullet \rightarrow \alpha\text{-}C_{10}H\text{-}NO_2 + \beta\text{-}C_{10}H_7NO_2 + C_{10}H_8 + HPF_6\,.$$

The quantitative compositions of the nitration products differ significantly in the two cases (Table 2). Compared with the direct nitration, the reactions of dimeric RC with $NO_2^\bullet$ are usually distinguished by greater regioselectivity. However, the RC of 1,4-dimethylnaphthalene gives rise to a high yield of 1,4-dimethyl-2-nitronaphthalene, whereas the nitration of 1,4-dimethylnaphthalene with acetyl nitrate or nitrogen tetroxide usually results in the preferential formation of the 5-nitro-derivative and the products of nitration in the methyl group. It must be emphasised that the conditions of the direct nitration of naphthalene hydrocarbons and their dimeric RC (temperature, acidity of the medium, composition of the ions present, etc.) have frequently differed significantly, which precludes in many instances final conclusions concerning the identity or non-identity of the regioselectivity of the two processes.

Monomeric RC of the naphthalene series are much more reactive than the dimeric RC.[66,67] One can therefore expect that they will recombine with $NO_2^\bullet$ faster than the dimeric RC and with a lower regioselectivity, which, however, may approach the selectivity of the usual nitration of naphthalene and its methyl derivatives. Unfortunately, an experimental test of this hypothesis is hindered by the extreme instability of this RC.

It has been suggested[64] that the reactivity of the RC with respect to $NO_2^\bullet$ decreases sharply with decrease in the electrochemical oxidation potentials of the corresponding ArH and of the RC of aromatic substrates having potentials less than 1.7 V relative to the normal hydrogen electrode do not interact with nitrogen dioxide. However, it has been shown[68] that the rates of reaction of the stable RC of tri-*p*-anisylamine and tri-*p*-bromophenylamine with an N_2O_4 solution are approximately the same despite the very large difference between the oxidation potentials of the corresponding amines (~0.7 V). The effective rate constants are 0.33 and 0.25 litre$^{1/2}$ mol$^{-1/2}$ s^{-1} at 20 °C (the reactions are of first order with respect to RC and of order 0.5 with respect to N_2O_4). Furthermore, the RC of tri-*p*-tolylamine proved to be much more reactive than the RC of tri-*p*-bromophenylamine (by a factor of 10^2),[68] whereas under conditions where the oxidation-reduction potential of the ArH/ArH^+ pair plays a decisive role one would expect the opposite relative reactivities of these RC. One cannot rule out the possibility of a parallel variation of the reactivity of the RC with respect to nitrogen dioxide and of their tendency to dimerise with formation of doubly protonated iaryls.

Nothing is known at present about the rate of reaction of highly active short-lived RC with $NO_2^\bullet$ in solution, but it has been established that in the gas phase such reactions are very rapid. The rate constant for the recombination of the dimeric RC derived from benzene with nitrogen dioxide is 2.4×10^{-11} cm^3 molecule^{-1} s^{-1} under these conditions.

The monomeric RC of toluene and *p*-xylene react somewhat more slowly and the reaction of the RC of naphthalene is much slower.[69,70]

The joint anodic oxidation of 1,4-dimethoxybenzene and the nitrite anion yielded 1,4-dimethoxy-2-nitrobenzene,[71] whose formation was explained by the recombination of the RC of 1,4-dimethoxybenzene with nitrogen dioxide:

$$p\text{-}CH_3OC_6H_4OCH_3 \xrightarrow{-e} p\text{-}CH_3OC_6H_4OCH_3^{+},$$

$$NO_2^- \xrightarrow{-e} NO_2,$$

$$p\text{-}CH_3OC_6H_4OCH_3^{+} + NO_2 \xrightarrow{-H^+} CH_3O\text{-}C_6H_3(NO_2)\text{-}OCH_3.$$

A parallel variation of the ease of substitution of a particular hydrogen atom by the nitro-group on treatment with $NO_2^{\cdot}$ and of the unpaired electron density at the corresponding carbon atom has been observed for the dimeric RC of naphthalene and 1,8-, 2,3-, and 2,6-dimethylnaphthalenes (see Table 2). More or less pronounced deviations from this type of variation occur for the RC of other naphthalene hydrocarbons.[64] These data justify the hypothesis that the distribution of the unpaired electron density on the RC is an important but not the only factor determining the isomeric composition of the nitro-products formed from the RC and nitrogen dioxide.

Table 3. Comparison of data for the nitration of aromatic compounds and the distribution of unpaired electron density in their RC.

ArH	Position in ArH at which nitration occurs preferentially	Position with maximum unpaired electron density in the RC
Benzonitrile	3 [74]	3 [75]
Nitrosobenzene	4 [76]	3 [77]
Benzoic acid	3 [74]	3 [75]
Toluene	4 [74]	4 [78]
Anisole	4 [74]	4 [79]
NN-Dimethylaniline	4 *	4 [80]
4,*NN*-Trimethylaniline	2 *	2 [81]
4-Methoxy-*NN*-dimethylaniline	2 *	2 [81]
4-Acetamido-*NN*-dimethylaniline	2 *	2 [81]
4-Carboxy-*NN*-dimethylaniline	2 *	2 [81]
4-Formyl-*NN*-dimethylaniline	2 *	2 [81]
4-Nitro-*NN*-dimethylaniline	2 *	2 [81]
4,4-Bis(dimethylamino)benzophenone	3 *	3 [81]
NNN'N'-Tetramethylbenzidine	3 [82]	3 [83]
Diphenylamine	4 *	4 [80]
Triphenylamine	4 [84, 85]	4 [80]
Naphthalene	1 [86]	1 [87]
Anthracene	9 [88]	9 [89]
Pyrene	1 [90]	1 [91]
Perylene	3 [92]	3 [89]
Azulene	1 [93]	1 [94]
Biphenylene	2 [38]	2 [95]
Furan	2 [96]	2 [97]
Pyrrole	2 [96]	2 [97]
Thiophen	2 [96]	2 [97]
Benzo-*p*-dioxin	2 [98]	2 [24]
Phenothiazine	3 [99]	3 [65]

*The data were taken from the handbook "Beilsteins Handbuch der organischen Chemie", Vierte Verlage, Springer Verlag, Berlin.

Note. Numbers in square brackets denote references (Ed. of Translation).

The partial addition of $NO_2^{\cdot}$ to the *unco*-positions in the RC apparently has an appreciable influence on the ratio of the nitro-isomers formed in a number of instances. Evidently, in such cases a greater or smaller proportion of the nitration products should be formed from the *unco*-σ-complex and the isomeric composition of the nitro-product does not reflect the true reactivities of the individual positions in the RC.

It is of interest to trace also the relation between the distribution of the unpaired electron density in the RC ArH^{+} and the position of the nitro-group in the nitration of ArH, such relation having been postulated previously.[72,73] The data in Table 3 (see also Table 2) show that the situation in this case is analogous to that examined above for the dimeric RC of the naphthalene series. Here too the most probable cause of the absence of an unambiguous relation between the unpaired electron density in the RC and the position of the nitro-group is the formation in the nitration reaction of *unco*-σ-complexes, which mask the true reactivities of the different positions in the ArH.[11] The complicating influence of this factor is apparently minimal for the positions in the ArH corresponding to the maximum unpaired electron density in the RC (Tables 2 and 3) and as a rule aromatic compounds are nitrated preferentially precisely in these positions. This rule can evidently be used to predict the positional selectivity in electrophilic aromatic nitration reactions.

One may predict the existence also of other factors which disturb the relation between the unpaired electron density in the RC and the positional selectivity of the nitration reaction. One of these factors can be seen in the nitration of secondary aromatic amines. *N*-Nitramines, which are converted into products of the nitration of the aromatic ring via the nitramine rearrangement, are intermediates in such reactions.[100] The preferential nitration of the amine in the *o*-position relative to the amino-group is usually a consequence of this mechanism,[101] although the unpaired electron density in the RC of aromatic amines is as a rule a maximum in the *p*-position (see Table 3). The unexpected nitration of nitrosobenzene in the *p*-position (in its RC, the unpaired electron density is a maximum in the *m*-position) is in all probability associated with the occurrence of the reaction via the intermediate formation of the hydrated form of the substrate.[102]

The coincidence of the most reactive position in the aromatic compound with the site where the maximum unpaired electron density is located in the RC, usually observed, creates additional possibilities for predicting the characteristic features of the electronic structure of the RC on the basis of data for the nitration of the corresponding ArH. For example, the nitration of vinylarenes in an unsaturated substituent[103,104] indicates an increased unpaired electron density in the vinyl group in the RC of vinylarenes. This is also indicated by the anomalous character of the dimerisation of such RC (unlike other RC of the type ArH^{+}, they dimerise via the exocyclic β-carbon atoms[105,106]) and by the result of a quantum-chemical calculation for the styrene RC.[107]

In the nitration of *m*-disubstituted benzenes in which one substituent is a powerful *ortho*- and *para*-directing agent and the other is a *meta*-directing agent, the influence of electron-donating substituents usually predominates.[108] It is natural to expect that the unpaired electron density in the RC of the aromatic compounds indicated will be a maximum in the *o*- and *p*-positions relative to the electron-donating group. The available data show that this is indeed the case. For example, for the RC of *NN*-dimethyl-3-nitroaniline,[81] the hyperfine interaction constant, which is directly proportional to the spin density is 5.9 and 6.3 G respectively for the *o*- and *p*-positions relative to the dimethylamino-group, while for the *m*-position it does not exceed 1.8 G.

The data examined indicate the possibility, in principle, of nitration via the intermediate formation of the RC, because they demonstrate that aromatic compounds can be converted

under the nitration conditions into the RC and the latter can be converted into nitro-compounds.

III. NITRATION OF AROMATIC COMPOUNDS BY THE NITRONIUM CATION

1. Nitration in the Gas Phase

Being a powerful oxidant,† the nitronium cation in the gas phase readily abstracts a single electron from the molecules of aromatic compounds such as benzene and its derivatives, converting them into the RC.[70,110] The subsequent recombination of the products of the one-electron transfer leads to a σ-complex, which is deprotonated on collision with molecules of bases B, forming the nitro-product.[70,111] Direct addition of the nitronium cation to benzene and its derivatives does not occur under these conditions:[70]

$$ArH + NO_2^+ \rightarrow ArH^{+\cdot} + NO_2^{\cdot} \rightarrow ArHNO_2^+ \xrightarrow[-BH^+]{B} ArNO_2$$

(here and henceforth B represents the base.) The electron transfer occurs in virtually every collision of the reacting species. The radical recombination stage is significantly slower and limits the rate of formation of the σ-complex.[70] The data presented confirm the validity of the quantum-chemical calculations,[7,112,113] indicating the possibility of electron transfer in nitration by the nitronium cation.

Thus, in the gas-phase nitration of aromatic compounds, the substrate RC is the primary reaction product and the σ-complex is the secondary product.

2. Nitration in Solution

The oxidising properties of the nitronium cation in solution can be characterised by the $NO_2^{\cdot}/NO_2^+$ oxidation-reduction potential, which is ~1.6 V in acetonitrile[114,115] and ~1.9 V in nitromethane[116] (relative to the normal hydrogen electrode). The rate of nitration of aromatic compounds by the nitronium cation increases with decrease in the ionisation potential, reaching a limit which is determined by the diffusion of the reacting species.[72,117] On the basis of the data of Coombes et al.,[117] the limiting ionisation potential can be estimated as being of the order of 8.8–9.0 eV.

The question of the mechanism of the liquid-phase nitration by the nitronium cation is at present controversial. Many experimental data obtained in the study of this reaction can be explained satisfactorily by a heterolytic mechanism in which the initial stage is the formation of the π-complex $ArH...NO_2^+$ with the nitro-group located at one of the π-bonds of the aromatic ring.[118] However, facts also exist which provide grounds for the hypothesis that the reaction can proceed via electron transfer.[9,13,60,74,113,118,119]

Perrin's communication,[60] which has aroused a lively discussion, quotes a number of arguments in support of the occurrence of this stage in the nitration of aromatic substrates more reactive than toluene by the nitronium cation. According to this study,[60] the reaction mechanism includes in this instance the formation of the short-lived radical pair $[ArH^+NO_2^{\cdot}]$ and its geminal recombination in the solvent cage:

$$ArH + NO_2^+ \rightarrow [ArH^+NO_2^{\cdot}] \rightarrow \underset{\sigma\text{-complex}}{ArHNO_2^+} \xrightarrow[-BH^+]{B} ArNO_2$$

One of the main arguments in support of this mechanism is that naphthalene is nitrated to give the usual mixture of mononitronaphthalenes in its oxidation at the anode in the presence of nitrogen dioxide.[60] It has been suggested that the nitration of naphthalene in the given instance is a result of the recombination of the naphthalene RC formed at the anode with $NO_2^{\cdot}$. However, it was soon established that this process proceeds virtually without the participation of the electrochemically generated RC.[62]

According to Eberson and Radner,[115] the nitration by the nitronium cation proceeds preferentially via the heterolytic (polar) pathway and only to an insignificant extent via the radical-ion pathway involving the outer-sphere electron transfer. It has also been suggested that, firstly, the relative contributions of these reaction pathways depend on the $ArH/ArH^{+\cdot}$ oxidation-reduction potential, and secondly, that the homolysis of the σ-complexes is an additional source of the $ArH^{+\cdot}$ RC and, thirdly, that the regioselectivities of the attack on ArH by the nitronium cation and on $ArH^{+\cdot}$ by nitrogen dioxide are in general different:

$$ArH + NO_2^+ \rightarrow \begin{cases} \rightarrow ArH^{+\cdot} + NO_2^{\cdot} \\ \quad \downarrow\uparrow \\ \rightarrow ArHNO_2^+ \xrightarrow[-BH^+]{B} ArNO_2 \end{cases}$$

Consequently, some of the nitro-products are formed, according to Eberson and Radner,[115] via the following reaction sequence:

$$\underset{(A)}{ArHNO_2^+} \rightarrow ArH^{+\cdot} + NO_2^{\cdot} \rightarrow \underset{(B)}{ArHNO_2^+} \rightarrow ArNO_2$$

where (A) and (B) are mixtures of isomeric σ-complexes differing in their composition. For this nitration pathway, the positions of the nitro-groups will be determined by the free-radical recombination stage and the set of the first two stages can be regarded as a kind of variant of the inner-sphere electron transfer.[120] There are a series of arguments in support of this view.

(1) The selectivity in the nitration of naphthalene by nitronium tetrafluoroborate ($\alpha/\beta \cong 15$) is not identical with the selectivity in the reaction between the dimeric napthalene RC and nitrogen dioxide ($\alpha/\beta \cong 40$).[51]

(2) The rate constants for the outer-sphere electron transfer from ArH to NO_2^+, calculated using the Marcus equation,[115] are much smaller than the corresponding rate constants for the nitration of ArH. The calculated constants depend on the $ArH/ArH^{+\cdot}$ oxidation-reduction potentials and vary within extremely wide limits (from ~10^{-16} litre mol^{-1} s^{-1} for benzene to ~10^6 litre mol^{-1} s^{-1} for ferrocene).

(3) The attempts to observe the chemically induced dynamic nuclear polarisation in nitration by the nitronium cation were unsuccessful.[121,122]

The different selectivity of the nitration in the $C_{10}H_8$–NO_2^+ and $(C_{10}H_8)_2^+$–$NO_2^{\cdot}$ systems apparently mean that the dimeric RC does not participate significantly in the nitration of naphthalene by the nitronium cation. However, this fact by itself does not justify the confident conclusion that the more reactive[66,67] monomeric naphthalene RC does not participate in the above reaction, because the selectivity in its recombination with nitrogen dioxide is unknown and there is no reason to suppose that it should be the same as that for the dimeric RC. Account must also be taken of the complex formation reaction between the nitronium cation and the solvent,[123,124] the decrease in the reactivity of NO_2^+ induced by this phenomenon (approximately by an order of magnitude[123]),

† The electron affinity of the nitronium cation can be estimated as being above 9 eV on the basis of the ionisation potential of nitrogen dioxide.[109]

and a probable change in the geometrical configuration of NO_2^+ on which the results of calculations of the rate constant for electron transfer between ArH and NO_2^+ depend decisively. It is also essential to take into account data[125] from which it follows that the rates of nitration of aromatic comounds by the nitronium cation may be appreciably lower than has usually come to be assumed (for example, at least by two orders of magnitude in the case of anisole).

The homolysis of σ-complexes is indeed possible. However, it is doubtful if this reaction can serve as an effective source of RC in the ArH–NO_2^+ systems: examination of data for the chemistry of the $ArHNO_2^+$ cation[126–132] creates the impression that these species are incapable of homolysis occurring readily enough to be able to compete with their deprotonation to nitro-derivatives.

According to Fukuzumi and Kochi,[74] like other electrophilic aromatic substitution reactions, nitration by the nitronium cation begins with the formation of a charge-transfer complex (CTC) between the reacting species, in which inner-sphere electron transfer takes place subsequently from the substrate of the reactant. The electron transfer is then regarded as a consequence of the thermal electronic excitation of the CTC, and the electronically excited state of the CTC is identified as the radical pair $[ArH^+E^\cdot]$:

$$ArH + E^+ \rightarrow ArH\cdots E^+ \xrightarrow{h\nu} [ArH^+E^\cdot] \rightarrow \underset{\sigma\text{-complex}}{ArHE^+} \rightarrow ArE + H^+$$

where E is the electrophile, including NO_2^+.

In particular, the linear dependence of the activation energy for electrophilic substitution on the energy of the charge-transfer bands in the spectrum of the complex $ArH\ldots E^+$ and also of the reaction constants ρ in the Brown equation on the quantities $\Delta h\nu_{st}/\Delta I$ characterising the rate of variation of the energy of the charge transfer band ($h\nu_{st}$) with the ionisation potential I of ArH supports this mechanism.[74]

The electron transfer mechanism described is analogous to that proposed previously.[133–136] From the standpoint of the ideas of the above investigators,[74,133–136] the thermal transfer of an electron thus proceeds analogously to its phototransfer. The most important difference consists in the fact that the electron phototransfer, being a Franck–Condon process, leads to the formation of a radical pair in a non-equilibrium unrelaxed state and therefore requires a much greater energy expenditure than the thermal transfer.[74,136–138] Comparison of the ArH/ArH^+ and $NO_2^\cdot/NO_2^+$ oxidation-reduction potentials[115] shows that, for aromatic compounds with low ionisation potentials, the energy levels of the complexes $ArH\ldots NO_2^+$ and $ArH^+\ldots NO_2^\cdot$ should be similar or that their ratio should be actually reversed.

The main reason why the calculation of the rate constants for the outer-sphere electron transfer from ArH to NO_2^+ leads to unduly low values of the latter is the appreciable energy of the reorganisation of the NO_2 group necessary for the electron transfer.[115] The component associated with the change in the internuclear angles of the NO_2 fragment on transition from the linear nitronium cation to the bent nitrogen dioxide molecule makes the dominant contribution to this energy. The unfavourable influence of this factor is apparently markedly weakened in electron transfer via the inner-sphere mechanism, since there is reason to believe that the NO_2 group then passes from the linear to the angular state already in the complex formation stage.[139] In general, the transition from the outer-sphere to the inner-sphere mechanism is frequently accompanied by a marked increase in the rate of electron transfer (up to by a factor of 10^9 [140]).

For aromatic amines, sulphides, and ethers, there exists yet another pathway to the formation of the radical pair $[ArH^+NO_2^\cdot]$, which has apparently not been discussed in the literature. The molecules of these compounds are attacked by the nitronium cation in the first place at the heteroatom having an unshared electron pair.[141] The homolysis of the ammonium, sulphonium, and oxonium cations formed under the conditions can evidently lead to the radical pair indicated:

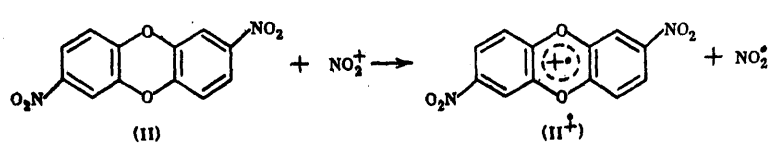
$$ArXR_n + NO_2^+ \rightarrow \underset{\underset{NO_2}{|}}{Ar\overset{+}{X}R} \rightarrow ArXR_n^{\cdot+} + NO_2^\cdot$$

X = N, O, S

The experimental confirmation of the possibility of the one-electron oxidation of aromatic compounds in the ArH–NO_2^+ system is hindered by the low stability of the RC, their ability to recombine with $NO_2^\cdot$, and, in particular, by the fact that in the case of the most active RC the recombination of the radical pairs $[ArH^+NO_2^\cdot]$ can apparently occur in the solvent "cage" without the emergence of the radicals into the bulk of the solution.

Examples of the oxidation of aromatic substrates to the RC by nitronium tetrafluoroborate have been described,[18,23,25] but one cannot be certain that the nitronium cation is in fact the oxidant in these reactions, since the reactant usually contains an admixture of the nitrosonium cation, which is difficult to separate and which is capable of oxidising these substrates

The results obtained for 2,7-dinitrodibenzo-*p*-dioxin (II) are of interest in this connection.[142] When compound (II) is treated with nitric acid in concentrated sulphuric acid, the radical-cation (II^+) is formed. Under these conditions, the nitrosonium cation does not oxidise the dioxin (II). Consequently a one-electron oxidant, superior in its strength to the nitrosonium cation, exists in the HNO_3–H_2SO_4 system (or can be formed in the presence of ArH). Since nitric acid is almost fully converted into the nitronium cation (the most reactive oxygen compound of nitrogen) under the conditions indicated above, it was concluded that the cation is responsible for the oxidation of the dioxin (II) to the RC:[142]



(II) (II^+)

The reaction discovered is the most convincing of experimental evidence for the ability of aromatic compounds to be oxidised in solution to the RC by the nitronium cation.

One can thus conclude that the role of the electron transfer in liquid-phase reactions involving the nitration of aromatic compounds by the nitronium cation is less clear than in the gas-phase reaction. However, here too there can be hardly any doubt about the possibility of the intermediate formation of the RC. Nevertheless the question of the extent to which the RC participates in these reactions is general and must still be regarded as open.

IV. CATALYTIC NITRATION

We shall now consider another large group of nitration reactions—the reactions occurring without the participation of the nitronium cation and catalysed by nitrous acid.# This nitration pathway is characteristic of aromatic compounds having fairly low ionisation potentials and activated with respect to electrophilic substitution.[3] The catalytic nitration reactions frequently occur under autocatalytic conditions, since the nitration catalyst is usually formed in the course of the reaction itself. In a pure form, they occur in media containing virtually no nitronium cations.

The mechanism of the catalytic reaction is often described in terms of a scheme involving nitration via nitrosation:[3]

$$ArH + HNO_2 \rightarrow ArNO + H_2O$$
$$ArNO + HNO_3 \rightarrow ArNO_2 + HNO_2, \text{ etc.}$$

It has been suggested that the initial formation and subsequant accumulation of nitrous acid in the ArH–HNO_2 systems occur as a result of the reduction of nitrous acid in oxidation-reduction side reactions. However, a number of experimental data, in particular the intermediate formation of the σ-complexes of $ArHNO_2^+$ in certain autocatalytic reactions[144,145] and also the preferential nitration of phenol in the *o*-position on treatment with dilute nitric acid (the nitrosation of this compound takes place almost exclusively in the *p*-position[146]) cannot be explained satisfactorily within the framework of this mechanism. Furthermore, there exist quite a few activated aromatic compounds§ whose nitrosation is unknown and many of them apparently do not enter into this reaction at all. Nevertheless, such compounds usually readily undergo autocatalytic nitration.

It has been shown recently that the autocatalytic nitration of *NN*-dimethylaniline[31] and phenol[147]—the classical substrates in the nitrosation reaction—and also naphthalene[148] cannot be explained in terms of the nitration mechanism involving reaction via nitrosation, at least in strong acids.

Two mechanisms are nowadays considered as the most probable. Firstly, one mechanism involves catalytic nitration initiated by the one-electron oxidation of the substrate,[31,40,145,148,149] whose possibility is due to the ability of the lower oxygen compounds of nitrogen ("nitrous acid") to effect the one-electron oxidation of activated aromatic compounds. The second mechanism involves nitration in which the active species is the electrophile $N_2O_4.NO^+$,[64] formed from nitrogen tetroxide and the nitrosonium cation.

The subsequent Sections will deal with the reactions involving the one-electron oxidation of aromatic compounds by the nitrosonium cation, their role in the formation of RC in the ArH–HNO_3 system and in autocatalytic nitration, and also the mechanism of nitration with participation of $N_2O_4.NO^+$.

1. The Nitrosonium Cation as a One-Electron Oxidant in Reactions with Aromatic Compounds

Until recently, the possibility of the one-electron oxidation of aromatic compounds by the nitrosonium cation had hardly been taken into account. This cation was regarded exclusively as a nitrosating agent interacting with aromatic substrates via a heterolytic mechanism. The limitations of this treatment became clear in recent years when the ability of the nitrosonium cation to accept one electron from the molecules of aromatic compounds has been demonstrated:

$$ArH + NO^+ \rightarrow ArH^+ + NO^\cdot$$

Reactions of this type were initially observed for readily oxidisable ArH of the amine type, namely phenothiazine,[150] phenoxazine,[40,151] *NNN'N'*-tetramethyl-*p*-phenylenediamine,[21] and derivatives of 9,10-dihydrophenazine.[21] It was later shown that polycyclic aromatic hydrocarbons also react similarly with NO^+.[18,22,115,152,153] For example, on reaction with nitrosonium perchlorate in trifluoroacetic acid, naphthalene is converted initially into the monomeric RC, then into the dimeric RC, and finally into a mixture of hydrocarbons having the polynaphthylene structure:[152,153]

$$C_{10}H_8 + NO^+ \rightarrow C_{10}H_8^+ + NO^\cdot$$
$$C_{10}H_8^+ + C_{10}H_8 \rightarrow (C_{10}H_8)_2^+$$
$$(C_{10}H_8)_2^+ \rightarrow \rightarrow C_{10}H_7 - (C_{10}H_6)_n - C_{10}H_7$$

In contrast to readily oxidisable substrates, naphthalene reacts with the nitrosonium cation fairly slowly, which can be explained by the endoergic character of the electron transfer in this case (calculation yields $\Delta G_0 = 13.1$ kcal mol^{-1} [115]). The reaction can be conveniently followed from the evolution of nitric oxide, whose yield is ~90% with respect to the initial nitrosonium salt.[153] These data show that the nitrosonium cation is almost incapable of nitrosating naphthalene.

Fluorene, triphenylmethane, and thiophen also interact with nitrosonium perchlorates with liberation of nitric oxide,[153] which indicates the one-electron oxidation of the substrates in these cases too. It is of interest that *NN*-dimethylaniline—an aromatic compound which readily undergoes electrophilic nitrosation—behaves in relation to the nitrosonium cation primarily as a one-electron reductant.[22,31]

Calculations by the Marcus equation of the thermodynamic kinetic characteristics of processes involving the one-electron oxidation of aromatic compounds by the nitrosonium cation[115] support the view that the formation of the RC is a result of the direct electron transfer from the π-system of the substrate to the electrophile.

Aromatic compounds of the benzen-type, which are oxidised with difficulty, hardly interact with the nitrosonium cation under the usual conditions (if one disregards the formation of a charge-transfer complex).[154,155] Calculations have shown[115] that the inertness of the nitrosonium cation with respect to such substrates is mainly due to thermodynamic causes (the oxidation-reduction equilibrium is very strongly displaced towards ArH and NO^+). It is therefore not surprising that the hexafluorophosphate of the hexafluorobenzene RC readily

---

All the lower oxygen compounds of nitrogen analytically determined as nitrous acids are designated for convenience by the term "nitrous acid".[143] The nitrosonium cation has come to be regarded as the most reactive component of nitrous acid.

§ Here and henceforth, this term is used to designate compounds containing aromatic nuclei activated with respect to electrophiles (aromatic amines, alkoxyarenes, polycyclic arenes, etc.).

reacts with nitric oxide, oxidising it to the nitrosonium cation:[156]

$$C_6F_6^+PF_6^- + NO^\cdot \rightarrow C_6F_6 + NO^+PF_6^-$$

In the gas phase the oxidising properties of the nitrosonium cation are more pronounced than in solutions and under these conditions it readily oxidises benzene to the RC.[157,158] The appreciable weakening of the oxidising properties of NO^+ in solution compared with the gas phase is caused by its strong solvation (the calculated hydration energy of NO^+ is ~80 kcal mol^{-1} [159]).

Other lower oxygen compounds of nitrogen can in all probability also function as one-electron oxidants in relation to aromatic compounds, because they frequently possess pronounced oxidising properties. For example, the electron affinity of nitrogen dioxide (3.1 eV [160]) is close to the electron affinity of powerful oxidants such as chlorine and bromine, while the calculated standard oxidation-reduction potential of the $NO_2^-/NO_2^\cdot$ pair is ~1 V in water.[161]

2. Autocatalytic One-Electron Oxidation of Aromatic Compounds by Nitric Acid

When aromatic compounds are oxidised to the RC by dilute nitric acid, which contains hardly any nitronium cations, the nitrosonium cation usually functions as the one-electron oxidant.[22,31,40,145,151,162] Reactions of this type are autocatalytic and are characterised by an induction period. The latter factor is caused by the absence of the nitrosonium cation from the reaction mixture in the initial period of the interaction. A special case of these reactions are those described by the overall equation[22,40,151]

$$3ArH + HNO_3 + 3H^+ \rightarrow 3ArH^+ + NO^\cdot + 2H_2O \quad (1)$$

For example, the oxidation of phenothiazine and phenoxazine by nitric acid in 57% perchloric acid, which leads to the RC perchlorates and nitric oxide in 75–80% yield, proceeds in accordance with this scheme.[40,151] Reactions (1) usually occur as independent reactions for the stoichiometric reactant ratio or in the presence of a deficiency of nitric acid. When an excess of HNO_2 is used, the nitration of ArH is usually observed.[22,28,29,40] The relatively unreactive forms of nitrous acid do not play a significant part in the oxidation of ArH, because in strong acids, where reactions (1) were carried out, they are converted into the nitrosonium cation.[163]

The reduction of dilute nitric acid by activated aromatic compounds is apparently similar to the cathodic reduction of this reactant, which is also autocatalytic.[164] Reactions (1) can be regarded as a kind of chain process in which the chain propagation stage is described by Eqns.(2) and (3):[40,165]

$$ArH + NO^+ \rightarrow ArH^+ + NO^\cdot \quad (2)$$

$$NO^\cdot + 0.5HNO_3 + 1.5H^+ \rightarrow 1.5NO^+ + H_2O \text{ , etc.} \quad (3)$$

The multiplication coefficient of the one-electron oxidant (NO^+) in this scheme is 1.5, which ensures the occurrence of one-electron oxidation with self-acceleration. The initial formation of the nitrosonium cation in the reaction mixture and hence the chain initiation take place in all probability as a result of the reduction by the aromatic substrate of the nitronium cation present at a vanishingly low concentration.

Eqn.(3) describes the autocatalytic regeneration of the nitrosonium cation from nitric oxide, which is the reverse of disproportionation of nitrous acid.[166,167] This process is catalysed by nitrous acid and proceeds with intermediate formation of nitrogen dioxide.[167]

In the case of unstable RC, the autocatalytic oxidation of ArH in accordance with Eqn.(1) is masked by the subsequent reactions of these radicals, for example, by their dimerisation. Dimeric products are obtained in the oxidation of *NN*-dimethylaniline,[22,31] 9-methylcarbazole,[40] and 1,3-diphenyl-2-pyrazoline [40] by nitric acid. As an example, we shall consider the reaction of *NN*-dimethylaniline with HNO_3 in 57% perchloric acid, which leads to the *NNN'N'*-tetramethylbenzidinium dication (IV) and nitric oxide in yields of ~80%:[22]

$$3C_6H_5N(CH_3)_2 + HNO_3 + 3H^+ \rightarrow 3C_6H_5\overset{+}{N}(CH_3)_2 + NO^\cdot + 2H_2O$$

$$2C_6H_5\overset{+}{N}(CH_3)_2 \rightarrow (CH_3)_2N\text{–}C_6H_4\text{–}C_6H_4\text{–}N(CH_3)_2 + 2H^+$$

(III)

$$3\,(III) + 2HNO_3 + 6H^+ \rightarrow 3\,(CH_3)_2\overset{+}{N}{=}C_6H_4{=}C_6H_4{=}\overset{+}{N}(CH_3)_2 + 2NO^\cdot + 4H_2O$$

(IV)

The overall reaction equation is

$$6C_6H_5N(CH_3)_2 + 4HNO_3 + 6H^+ \rightarrow 3\,(IV) + 4NO^\cdot + 8H_2O$$

Anthracene reacts with nitric acid in 57% perchloric acid in a manner different from that of the reactions of *NN*-dimethylaniline, 9-methylcarbazole, and 1,3-diphenyl-2-pyrazoline, affording anthraquinone as the final product. The initial stage of the reactions is probably the same as for the compounds quoted above:[22]

$$3C_{14}H_{10} + HNO_3 + 3H^+ \rightarrow 3C_{14}H_{10}^+ + NO^\cdot + 2H_2O$$

This is supported by the formation of nitric oxide from nitric acid in a high yield. The anthracene RC is converted into anthraquinone as a result of its interaction with water in the presence of an excess of the oxidant.[168–170] The ability of NO^+ to oxidise anthracene to the RC has been established.[115] An analogous interpretation of the formation of anthraquinone in the nitration of anthracene with nitrogen tetroxide has been given in another study.[171]

The analogy between the autocatalytic one-electron oxidation of activated aromatic compounds by nitric acid and the reactions involving the oxidation of certain inorganic substances by the same reagent is striking. The dissolution of metallic silver on interaction with nitric acid in 57% perchloric acid[40] and the oxidation of bivalent iron to the tervalent state[172] can serve as examples of such processes:

$$3Ag + HNO_3 + 3H^+ \rightarrow 3Ag^+ + NO^\cdot + 2H_2O$$
$$3Fe^{2+} + HNO_3 + 3H^+ \rightarrow 3Fe^{3+} + NO^\cdot + 2H_2O$$

3. Autocatalytic Nitration Initiated by One-Electron Oxidation

The mechanism of nitration of this type involves two coupled stages: the autocatalytic oxidation of the aromatic compound to the RC and the conversion of the RC into the nitro-product as a result of its recombination with nitrogen dioxide.[31,40,145,148,165] The autocatalytic character of these reactions therefore arises in the one-electron oxidation stage, in the course of which an electron is transferred from the aromatic substrate to the nitrosonium cation or to some other form of nitrous acid.

When the conditions in the interaction of the reactants do not favour the recombination of the RC with nitrogen dioxide, the reactions occurring in the ArH–HNO_3 system are restricted to the one-electron oxidation of the aromatic compound. As already mentioned, the formation of the nitro-products is promoted by the use of an excess of nitric acid.

Such influence by the excess of the reagent can be accounted for by the increase in the concentration of nitrogen dioxide in the reaction mixture as a consequence of the more effective absorption of nitric oxide by nitric acid. In the ideal case, where they entire nitric oxide formed in accordance with Eqn.(1) is oxidised to the dioxide, the one-electron oxidation of ArH can be described by Eqn.(4) and the autocatalytic nitration can be described by Eqns.(4) and (5):

$$ArH + HNO_3 + H^+ \rightarrow ArH^{\cdot+} + NO_2^{\cdot} + H_2O \quad (4)$$

$$ArH^{\cdot+} + NO_2^{\cdot} \rightarrow ArNO_2 + H^+ \quad (5)$$

According to the literature,[31,149] the autocatalytic nitration reactions initiated by the one-electron oxidation are of first order with respect to the substrate, although a fractional order has been quoted (1.5).[148] The order with respect to nitric acid is variable, diminishing with increase in its concentration from 1 to 0.[31,148,149] This finding has been explained by the change of the rate-limiting stage when the reactant concentration is altered. At higher concentrations, the electron transfer from ArH to the one-electron oxidant becomes such a stage, while at low concentrations the oxidation of nitric oxide by nitric acid becomes rate-limiting.

The mechanism of the autocatalytic nitration initiated by the one-electron oxidation corresponds to a true autocatalytic process, since in this case the accumulation of the catalyst does not require the occurrence of any side reactions. In this respect, it differs from the mechanism involving nitration via nitrosation, in which the accumulation of nitrous acid can be achieved only as a result of side reactions.

The nitration of *NN*-dimethylaniline by nitric acid in 75–80% sulphuric acid is an example of an autocatalytic reaction which exhibits a number of specific features.[31] These include a fairly high concentration of the nitronium cation in the reaction mixture and the complete protonation of the initial amine. The reaction products are mainly *NN*-dimethyl-*p*-nitroaniline and nitroderivatives of *NNN'N'*-tetramethylbenzidine in proportions which depend on the acidity of the medium. The base, formed apparently as a result of the unusual deprotonation of the protonated amine by the nitrosonium cation, enters into the reaction.[31] A nitration mechanism with participation of not only the nitrosonium cation but also of the nitronium cation has been proposed:

It is noteworthy that this mechanism can be only specific in character. In principle, it is applicable solely to the nitration of sufficiently basic aromatic compounds which are almost wholly protonated under the reaction conditions. If the reaction mixture contains an appreciable concentration of the non-protonated substrate, then evidently in this case the substrate can react mainly with the nitronium cation, which is more reactive as an electrophile than the nitrosonium cation by ~14 orders of magnitude.[173]

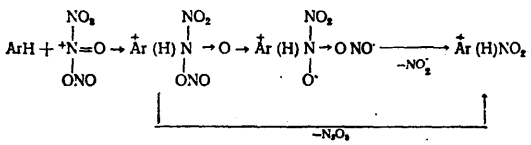
The products of the autocatalytic nitration of *NN*-dimethylaniline,[174] *p*-nitrophenol,[175,176] mesitylene,[122] and durene[177] (labelled with $H^{15}NO_3$ nitric acid) in sulphuric or trifluoroacetic acid exhibit a chemically induced dynamic polarisation of the ^{15}N nuclei, which has been explained by the formation of nitro-derivatives from the radical pairs $[ArH^{\cdot+}NO_2^{\cdot}]$.

There is now no doubt that the autocatalytic one-electron oxidation of ArH can be the initial stage of the autocatalytic nitration of activated aromatic compounds.

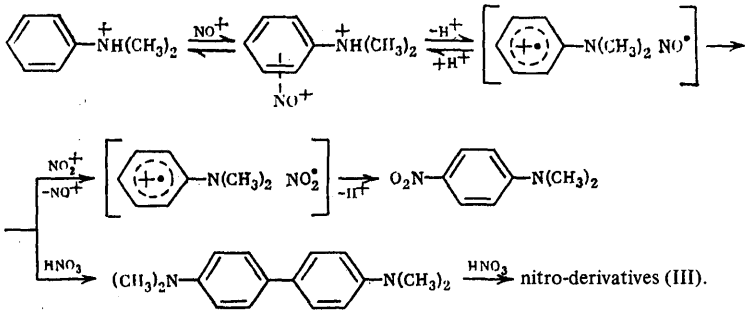
4. The Mechanism of the Autocatalytic Nitration with Participation of $N_2O_4.NO^+$

A new mechanism has been proposed recently for the autocatalytic nitration catalysed by the cation $N_2O_4.NO^+$ [64,178] whose existence has not so far been confirmed. It is assumed that this cation, tentatively formed from nitrogen tetroxide and the nitrosonium cation, is directly involved as the nitrating species:

$$N_2O_4 + NO^+ \rightarrow N_2O_4 \cdot NO^+$$



$$\overset{+}{Ar}(H)NO_2 + N_2O_3 \rightarrow ArNO_2 + HNO_2 + NO^+$$



(III)

The oxidation of nitrous acid by nitric acid regenerates nitrogen tetroxide (and hence also the catalyst). The above mechanism explains the chemically induced dynamic nuclear polarisation effect in the catalytic nitration reactions by the intermediate formation of radical pairs in the homolysis of the primary σ-complex at the N–O bond.

The determination of the applicability of the mechanisms examined evidently required further studies. Nevertheless, it is already clear that the mechanism involving nitration via nitrosation can be excluded from consideration for catalytic nitration reactions of a number of aromatic hydrocarbons (for example, naphthalene), since such compounds are either hardly nitrosated or they react with nitrosating agents too slowly.

V. THE CHANGE IN THE MODE OF REACTION AFTER A CHANGE IN THE REACTANT RATIO

As already mentioned, in certain cases the use of a deficiency of the nitrating agent makes the RC of the substrate the final product of the reaction of the latter. This is associated with the uncoupling of the multistage radical-ion nitration process in the part of the mechanism between the first and subsequent stages, which is induced by unfavourable conditions for the conversion of the RC into the nitration product. The influence of this factor decreases rapidly with increase in the mole fraction of the reactant in the initial reaction mixture. This can result in an additional change in the composition of the reaction product corresponding to the transition from the one-electron oxidation to nitration after a comparatively small change in the reactant ratio.[22,25,28,29]

A characteristic example is provided by the nitration of dibenzo-*p*-dioxin (V) in trifluoroacetic acid.[25] For the reagent : substrate molar ratio $n \geq 2$, this compound reacts rapidly with nitric acid, being converted into a mixture of 2,7-dinitrodibenzo-*p*-dioxin (VI) and 2,8-dinitrodibenzo-*p*-dioxin (VII) in a high yield. The nitration is accompanied by the appearance of a rapidly vanishing blue colour characteristic of the RC ($V^{+\cdot}$). On the other hand, for $n = 0.3–0.5$, the RC is the final reaction product (in ~90% yield). The range of values of n from 2 to 0.5 corresponds to a smooth transition from nitration to one-electron oxidation:

For a specified value of n, variation of the concentrations of the starting materials does not entail significant changes in the ratio of the RC and the nitro-compounds.

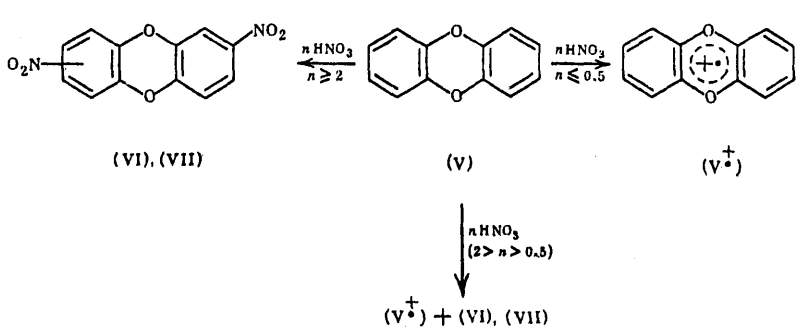
The fact that the dinitro-derivatives (VI) and (VII) are also formed in the presence of a deficiency of nitric acid implies that the introduction of the second nitro-group is faster than that of the first. This anomaly can apparently be explained by the higher reactivity of the RC of the mononitro-derivative of dioxin compared with ($V^{+\cdot}$) under conditions where the introduction of both groups is limited by the rates of recombination of the above RC with $NO_2^{\cdot}$.

A mixture of the dinitro-compound (VI) and (VII) is obtained also in the reaction of a known salt of the radical-cation ($V^{+\cdot}$) with nitrogen dioxide.[25] The introduction of the second nitro-group is undoubtedly catalysed in this case by the strong acid formed in the RC mononitration stage (cf. Eberson et al.[62]).

In the nitration of compound (V) by nitrogen tetroxide in trifluoroacetic acid, the same features are observed as in the nitration with nitric acid.[25] For the reagent : substrate molar ratio $n = 0.25$, the RC ($V^{+\cdot}$) formed is stable, while for $n \geq 1.5$, it is converted into a mixture of the nitro-compounds (VI) and (VII) in a high yield. The values of n between 0.25 and 1.5 constitute an intermediate region. The limiting value $n = 1.5$ corresponds to the stoichiometry of the dinitration of aromatic compounds by nitrogen tetroxide.[25,179]

A radical-ion mechanism has also been proposed for the nitration of aromatic compounds by nitrogen tetroxide in neutral solvents. It has been suggested that the initial stage of the nitration involving this mechanism is the oxidation of the substrate to the RC by nitrogen dioxide.[171] However, it has been suggested[64] that the operation of this mechanism is unlikely because nitrogen dioxide is a poor one-electron oxidant (the electron exchange in the $NO_2^{\cdot}–NO_2^-$ system is relatively slow). The formation of the RC when aromatic compounds having pronounced reducing properties are acted upon by nitrogen tetroxide can be explained[64] by the oxidation of ArH by the nitrosonium cation arising as a result of the isomerisation of N_2O_4 to the nitrosyl nitrate form.

A dependence of the composition of the reaction product on the reagent : substrate ratio, analogous to that examined above, obtains also in the nitration of phenothiazine,[28,29] *N*-methylphenoxazine,[22] and probably *NN*-dimethylaniline[22] by nitric acid.



VI. NITRATION OF AROMATIC COMPOUNDS BY TETRANITROMETHANE AND METAL NITRATES

1. Thermal Nitration by Tetranitromethane

Tetranitromethane (TNM) is a mild nitrating agent[180] and a moderately strong oxidant (electron affinity 1.3 eV,[180] electrochemical reduction potential in methanol 0.7 V,[181] calculated oxidation-reduction potential in water 0.9 V relative to the normal hydrogen electrode[182]).

The interaction of aromatic compounds with TNM begins in all probability with electron transfer from the substrate to the reagent within the ArH...TNM CTC:

$$ArH + C(NO_2)_4 \rightarrow ArH\cdots C(NO_2)_4 \rightarrow ArH^{+}C(NO_2)_4^{-}$$

The decomposition of the TNM radical-anion formed leads to nitrogen dioxide,[180] which subsequently reacts with the RC and the excess substrate:

$$C(NO_2)_4^{-} \rightarrow C(NO_2)_3^{-} + NO_2^{\cdot}$$

$$ArH^{+} + NO_2^{\cdot} \xrightarrow{-H^{+}} ArNO_2$$

The rate-limiting stage of the nitration can be both electron transfer and the conversion of the RC into the nitro-product. The latter variant is most favourable for demonstrating the reaction mechanism and obtains in the case of the least active RC.

An example of the reactions in which electron transfer is not the rate-limiting stage is provided by the nitration of *N*-methylphenoxazine (VIII).[22,26] In this reaction, the initial aromatic compound is oxidised rapidly and with a high yield to the RC, which is subsequently converted comparatively slowly into *N*-methyl-3-nitrophenoxazine (IX).

The Figure presents the spectra of the (VIII)–TNM system in the visible region, demonstrating the conversion of the RC into the nitro-compound. The presence of the isosbestic point confirms the conclusion that the RC is located on the nitration coordinate. The nitro-compound (IX) can also be obtained by treating a known salt of the RC ($VIII^{+\cdot}$) with nitrogen dioxide or TNM.[22]

It is noteworthy that the reaction of the oxazine (VIII) with TNM is the first example of nitration where direct evidence has been obtained for the intermediate formation of the substrate RC and it has been shown that this nitration pathway is the main one.

The reactions of TNM with the phenyl derivatives of magnesium, tin, and mercury are also of the oxidation-reduction type, but in this case the aromatic compounds are hardly nitrated. The main product of these reactions is benzene.[183,184] The above finding has been explained by the specific properties of the organometallic RC, namely by their ability to fragment readily with formation of neutral free radicals.[183,184] The fragmentation is so rapid that there is insufficient time for the RC to recombine with nitrogen dioxide:

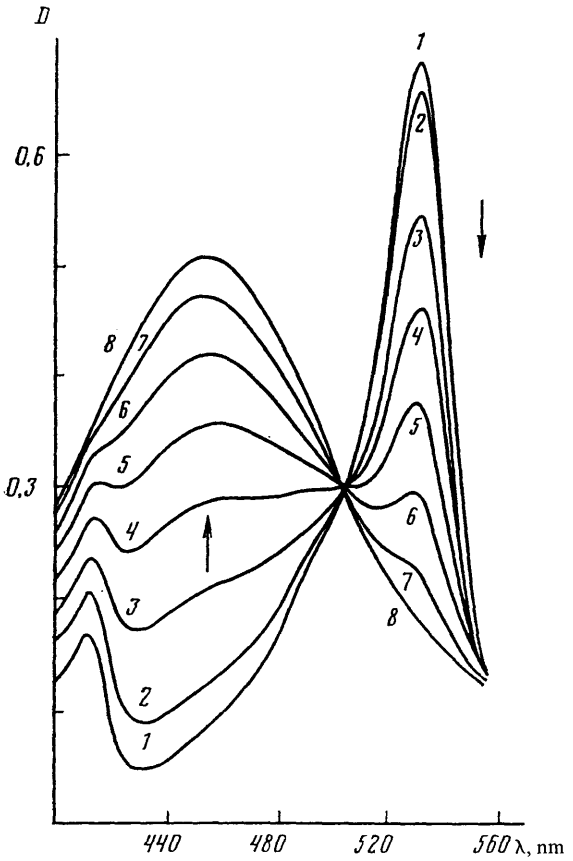
$$C_6H_5M + C(NO_2)_4 \rightarrow C_6H_5M^{+} + C(NO_2)_4^{-} \rightarrow C_6H_5^{\cdot} + M^{+}C(NO_2)_3^{-} + NO_2^{\cdot}$$

$$C_6H_5^{\cdot} \xrightarrow{Solv} C_6H_6$$

$$C_6H_5^{\cdot} + NO_2^{\cdot} \rightarrow C_6H_5NO_2$$

$M = C_6H_5Mg$, C_6H_5Hg, $(C_6H_5)_3Sn$; Solv = solvent.

The low yield of nitrobenzene indicates a low probability of the recombination of the radicals $C_6H_5^{\cdot}$ and $NO_2^{\cdot}$ in solutions.[183,184]



Electronic absorption spectra describing the conversion of the *N*-methylphenoxazine RC into *N*-methyl-3-nitrophenoxazine on nitration of *N*-methylphenoxazine with TNM in 97% acetic acid.[22] The absorption band with λ_{max} = 412 and 533 nm are due to the RC and that at 450 nm is due to the nitro-derivative. The initial concentrations of the reagent and the substrate were 5×10^{-3} and 5×10^{-4} M respectively; the thickness of the cell l = 0.1 cm. Spectra recorded under the following conditions: 1) 1 min after mixing the initial solutions; 2) after 2.5 min; 3) after 21 min; 4) after 51 min; 5) after 1 h 27 min; 6) after 2 h 7 min; 7) after 2 h 54 min; 8) after 3 h 53 min.

2. Photochemical Nitration with Tetranitromethane

Under the usual conditions, TNM does not react with aromatic compounds difficult to oxidise such as benzene, naphthalene, etc. or reacts with them very slowly.[185] However, it readily forms charge-transfer complexes with these compounds, whose irradiation with light at the wavelength corresponding to the charge-transfer band leads to the electron transfer:[186]

$$ArH + C(NO_2)_4 \rightarrow ArH\cdots C(NO_2)_4 \xrightarrow{h\nu} [ArH^{+}C(NO_2)_3^{-}] + NO_2^{\cdot}$$

One may therefore expect that nitration of the relatively unreactive ArH would be accelerated in the light. It has been shown for *N*-ethylcarbazole [187] that such influence by light does indeed occur.

The photochemical nitration of anthracene with TNM leads to a 9-nitroanthracene, which has been explained by the recombination of the 9-anthryl free radical with $NO_2^{\cdot}$.[188] However, one cannot rule out the possibility that the anthracene RC, whose formation in the course of the reaction is not open to doubt, in contrast to the 9-anthryl radical, participates in the formation of the nitro-derivative together with nitrogen dioxide.[188]

3. Nitration with Metal Nitrates

Among all the metal nitrates, the strongest nitration agents are salts with pronounced oxidising properties[189–196] such as titanium(IV), zirconium(IV), iron(III), and copper(II) nitrates and cerium ammonium nitrate. Some of these salts are such powerful oxidants that under the usual conditions they oxidise even alkanes[193] and water.[195]

The study of the nitration of aromatic compounds with titanium(IV) nitrate led to the conclusion that the nitrate salt is involved directly in the reaction.[191] Under comparable conditions, anhydrous metal nitrates can be superior to nitric acid as regards their nitrating capacity.[191,192] These facts indicate that nitration with metal nitrates can proceed via a specific mechanism and not necessarily via a trivial pathway involving the hydrolysis of the salt.

According to a recently proposed mechanism,[197] in the nitration of arenes by cerium ammonium nitrate,[192] the nitronium cation, formed in the interaction of the initial compounds, is the active species. Together with nitration, the oxidation of arenes to the RC by the cerium(IV) cation,[198] which is regarded as a side reaction,[197] has also been noted. However, the question of the role of the RC in such reactions and even more so in nitration by metal nitrates is not in general quite so simple, because there is a possibility of the formation of nitro-products from the RC when they interact with nitrate anions:

$$ArH + M(NO_3)_n \rightarrow ArH^{+}NO_3^{-} + M(NO_3)_{n-1}$$
$$ArH^{+} + NO_3^{-} \rightarrow \rightarrow ArNO_2$$

Such a nitration mechanism has been proposed in a study[199] of the nitration of *N*-methylphenoxazine (VIII). Heating of this compound in propanol with iron(III) or copper(II) nitrate leads to a satisfactory yield of the 3-nitro-derivative (IX). The formation of the phenoxazine RC is observed in the cold. The known radical-cation salt ($VIII^{+}\cdot ClO_4^{-}$) also gives rise to the nitro-compound (IX) on heating in propanol with tetrapropylammonium or potassium nitrate.

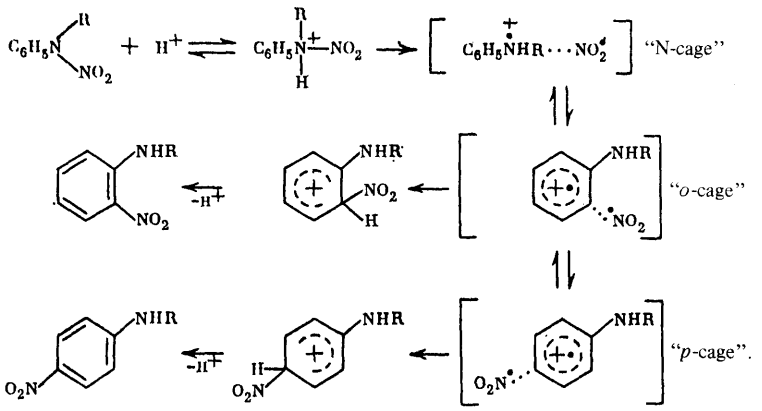
A number of facts indicate indirectly that this nitration pathway is possible also for other aromatic compounds. For example, it has been shown that the one-electron oxidation of benzene by cobalt(III) trifluoroacetate in the presence of potassium nitrate leads to nitrobenzene.[200] The electrochemical oxidation of anthracene in the presence of the tetrabutylammonium nitrate supporting electrolyte as the potential corresponding to the oxidation of anthracene to the RC affords a mixture of 9-nitro-, 9,10-dinitro-, and 4,9-dinitro-anthracene.[201] Under these conditions, the supporting electrolyte is oxidised only at an appreciably higher potential.

Although the mechanism of the conversion of the RC into nitro-compounds on interaction with NO_3^{-} is as yet not clear, the very fact of the occurrence of such reactions is not open to doubt. One of them has been described in a study[202] where it was shown, in an investigation of the action of nucleophiles on the RC of dibenzo-*p*-dioxin, that treatment of the perchlorate salt of this RC with potassium nitrate leads to 2-nitrodibenzo-*p*-dioxin. In contrast to the RC of dibenzo-*p*-dioxin, the thianthrene RC, which has a similar structure, reacts with the nitrate anion to form thianthrene *S*-oxides.[203]

The nitration of aromatic compounds by palladium nitrate proceeds via a specific mechanism, which is indicated by the unusually high level of *m*-substitution in the nitration of toluene and chlorobenzene by this reagent.[204] The partial rate factors for the attack of toluene by $Pd(NO_3)_2$ are 0.3 (*o*), 1.3 (*m*), and 3.0 (*p*). The partial rate factors for the palladisation of toluene by bivalent palladium salts are close to these values:[205] 0.28–0.95 (*o*), 1.44–1.87 (*m*), and 1.64 to 4.47 (*p*). It is logical to suppose that the nitration of aromatic substrates by palladium nitrate involves the intermediate formation of organopalladium compounds.

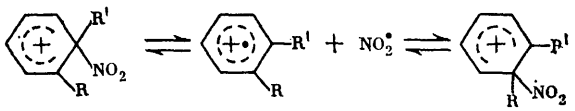
VII. THE RADICAL-ION MECHANISM OF THE NITRAMINE REARRANGEMENT AND THE ISOMERISATION OF NITROARENIUM CATIONS

The radical-ion mechanism of the nitramine rearrangement, involving the homolysis of the protonated form of nitramine with formation of the amine RC and nitrogen dioxide followed by the recombination of these radicals, has been justified in a number of studies:[206–209]



This mechanism is supported by the observation of the CIDNP effect in one of the reactions of the type considered[210] and also by the results of measurements of the $^{15}N/^{14}N$ and $^{14}C/^{12}C$ kinetic isotope effects.[211]

The isomerisation of the nitroareneium cations $ArRNO_2^+$ with the migration of the nitro-group along the perimeter of the aromatic ring is usually regarded as an intramolecular process.[132] However, one cannot rule out the possibility that in certain cases it can proceed via a radical-ion pathway similar to the mechanism of the nitramine rearrangement:[60]



From the standpoint of thermodynamics, the homolysis of nitroarenium cations is preferable to the alternative pathway involving their dissociation into ArH and NO_2^+ in those cases where the ArH have fairly low ionisation potentials. This conclusion is based on the results of the calculation of the ΔG_0 corresponding to electron transfer from various aromatic compounds to the nitronium cation.[115] The possibility of the radical-ion pathway leading to the isomerisation of nitroarenium cations is supported by data for the capacity for homolysis.[212] However, it is not as yet clear whether this reaction pathway can be the main one.

---o0o---

Thus studies in recent years have shown that the ideas about electrophilic nitration according to which it is a purely heterolytic process can no longer claim to be universal. An increasing number of facts have been appearing which do not fit within the framework of these ideas and which show that radical species such as radical-cations and nigrogen dioxide can play an important role in nitration. On the other hand, these facts do not conflict with the classical mechanism of nitration as regards the role of the σ-complexes as the direct precursors of the nitro-derivatives. For practical purposes, it is extremely significant that free radicals serve as a source of not only nitro-products but also (by virtue of their high reactivity) of various side products. It is not difficult to note that the observed evolution of ideas about the nitration mechanism is a specific manifestation of the more general trend towards a separation of the concepts of heterolytic and electrophilic (nucleophilic) substitution. As a result, the fact that a reaction belongs to the class of electrophilic (nucleophilic) substitution reactions is no longer a basis for its automatic inclusion in the series of heterolytic reactions. In the field of nucleophilic aromatic substitution reactions, this has been reflected, in particular, by the establishment of the $S_{RN}1$ radical-nucleophilic substitution mechanism.

The studies designed to discover the role of electron transfer in nitration are naturally far from being completed. One can suppose that they will ultimately lead to the development of clear experimental criteria for a radical-ion mechanism and will provide an answer to the question of its specific contribution in the overall set of aromatic nitration reactions.

During the preparation of the article for publication, a series of new studies concerning the role of the oxidation-reduction stage in nitration reactions have been published, in particular a monograph[213] and a review,[214] which contain sections devoted to these reactions. It has been shown[215] that the regioselectivity of the nitration of naphthalene with nitric acid in trifluoroacetic acid, expressed by the ratio α : β of the mononitronaphthalenes formed, depends significantly on temperature and, when the latter is reduced, it reaches values characteristic of the recombination of the dimeric naphthalene radical-cation with nitrogen dioxide. This fact and also the detection of the radical-cation indicated above in the $C_{10}H_8$–HNO_3–CF_3COOH system have been interpreted as evidence for the radical-ion mechanism of the nitration of naphthalene.

The complex oxidation reactions occurring in the interaction of a series of compounds of the dihydropyridine series with nitric acid have been explained by the oxidation of these compounds to the RC and the recombination of these species with nitrogen dioxide via the oxygen atom of the latter.[216]

The mechanism of the nitration of aromatic compounds by nitrogen tetroxide, whose initial stage is the heterolysis of N_2O_4 to form the nitrosonium cation, has been discussed.[217] Other pathways leading to nitration by this reagent presumably involve its homolysis to nitrogen dioxide. The latter can oxidise aromatic substrates to the RC,[218,219] which, as already mentioned, are capable of being converted into nitrocompounds under the influence of $NO_2^{\cdot}$. It has been demonstrated by pulse methods[218,219] that the electron transfer from *NNN'N'*-tetramethylbenzidine, *N*-methylphenothiazine, and metiazinic acid to $NO_2^{\cdot}$ in polar medium is extremely fast: the corresponding rate constants are of the order of 10^7–10^8 litre mol^{-1} s^{-1}. According to the available data,[178] there is also a possibility of the free-radical attack on aromatic substrates by nitrogen dioxide, characterised by a low positional selectivity and also leading to nitro-derivatives.

REFERENCES

1. K.A.Bilevich and O.Yu.Okhlobystin, Uspekhi Khim., 1968, **37**, 2162 [Russ.Chem.Rev., 1968(12)].
2. L.Eberson, Adv.Phys.Org.Chem., 1982, **18**, 79.
3. R.W.Hoffmann, "Elucidation of Reaction Mechanisms" (Translated into Russian), Izd.Khimiya, Moscow, 1979, p.22.
4. J.Kenner, Nature, 1945, **156**, 369.
5. J.Weiss, Trans.Faraday Soc., 1946, **42**, 116.
6. L.Horner and F.Hubbenett, Annalen, 1953, **579**, 193.
7. S.Nagakura and J.Tanaka, J.Chem.Phys., 1954, **22**, 563.
8. C.K.Ingold, "Structure and Mechanism in Organic Chemistry" (Translated into Russian), Izd.Mir, Moscow, 1973.
9. O.Yu.Okhlobystin, "Perenos Elektrona v Organicheskikh Reaktsiyakh" (Electron Transfer in Organic Reactions), Izd.Rostov.Gos.Univ., Rostov-on-Don, 1974, p.91.
10. V.A.Koptyug, "Arenonievye Iony (Stroenie, Reaktsionnaya Sposobnost')" [Arenium Ions (Structure and Reactivity)], Izd.Nauka, Novosibirsk, 1975, p.163.
11. V.A.Koptyug, Zhur.Vses.Khim.Obshch.im.Mendeleeva, 1976, **21**, 247.

12. A.V.Todres, Uspekhi Khim., 1978, **47**, 260 [Russ. Chem.Rev., 1978(2)].
13. I.P.Beletskaya, Zhur.Vses.Khim.Obshch.im.Mendeleeva, 1979, **24**, 148.
14. L.I.Belen'kii and V.P.Gul'tyai, Khim.Geterotsikl. Soed., 1981, 723.
15. V.D.Pokhodenko, L.S.Dyagtyarev, V.G.Koshechko, and V.S.Kuts, "Problemy Khimii Svobodnykh Radikalov" (Problems of the Chemistry of Free Radicals), Izd.Naukova Dumka, Kiev, 1984, p.146.
16. A.F.Pozharskii, "Teoreticheskie Osnovy Khimii Geterotsiklov" (Theoretical Foundations of the Chemistry of Heterocycles), Izd.Khimiya, Moscow, 1985, p.172.
17. H.Suzuki, Synthesis, 1972, p.217.
18. A.S.Morkovnik, N.M.Dobava, O.Yu.Okhlobystin, and V.V.Bessonov, Zhur.Neorg.Khim., 1981, **17**, 2618 [Russ.J.Inorg.Chem., 1981(10)].
19. V.D.Pokhodenko, V.A.Khizhnyi, V.G.Koshechko, and O.I.Shkrebtii, Zhur.Neorg.Khim., 1975, **11**, 1873 [Russ.J.Inorg.Chem., 1975(7)].
20. A.S.Morkovnik, N.M.Dobaeva, V.B.Panov, and O.Yu.Okhlobystin, Dokl.Akad.Nauk SSSR, 1980, **251**, 125.
21. V.G.Koshechko, A.N.Inozemtsev, and V.D.Pokhodenko, Zhur.Org.Khim., 1981, **17**, 2608.
22. N.M.Dobaeva, Candidate's Thesis in Chemical Sciences, Rostov State University, Rostov-on-Don, 1982.
23. A.S.Morkovnik, N.M.Dobaeva, E.Yu.Belinskii, and O.Yu.Okhlobystin, Zhur.Vses.Khim.Obshch.im. Mendeleeva, 1981, **26**, 461.
24. M.Tomita and S.Ueda, Tetrahedron Lett., 1963, 1189.
25. A.S.Morkovnik, E.Yu.Belinskii, N.M.Dobaeva, and O.Yu.Okhlobystin, Zhur.Org.Khim., 1982, **18**, 378.
26. A.S.Morkovnik, N.M.Dobaeva, and O.Yu.Okhlobystin, Khim.Geterotsikl.Soed., 1982, 122.
27. A.S.Morkovnik, V.B.Panov, D.M.Elisevich, and V.V.Mezheritskii, Zhur.Org.Khim., 1983, **19**, 1984.
28. A.S.Morkovnik, N.M.Dobaeva, and O.Yu.Okhlobystin, Khim.Geterotsikl.Soed., 1980, 1135.
29. A.S.Morkovnik, N.M.Dobaeva, and O.Yu.Okhlobystin, Khim.Geterotsikl.Soed., 1981, 1214.
30. K.Sehested and J.Holcman, Nucleonika, 1979, **24**, 941.
31. J.C.Giffney and J.H.Ridd, J.Chem.Soc., Perkin Trans.II, 1979, 618.
32. V.A.Bushmelev and V.A.Koptyug, Zhur.Org.Khim., 1969, **5**, 703.
33. A.Fischer and C.C.Greig, Canad.J.Chem., 1978, **56**, 1063.
34. M.M.Nafissi, D.P.Koharski, M.S.Puar, and A.T.McPhail, J.Org.Chem., 1982, **47**, 3345.
35. A.M.Crossley and C.H.Hampshire, J.Chem.Soc., 1911, 721.
36. I.Puskas and E.K.Fields, J.Org.Chem., 1967, **32**, 589.
37. I.Puskas and E.K.Fields, J.Org.Chem., 1967, **32**, 3924.
38. W.Baker, J.W.Barton, and J.F.W.McOmie, J.Chem. Soc., 1958, 2666.
39. R.Marquis, Ann.chim.phys., 1905, **4**, 196.
40. A.S.Morkovnik, Zhur.Obshch.Khim., 1982, **52**, 1877.
41. H.Hodgson and G.Turner, J.Chem.Soc., 1942, 584.
42. J.M.Hornback and H.E.Gossage, J.Org.Chem., 1985, **50**, 541.
43. G.A.Golubeva, Yu.N.Portnov, A.N.Kost, et al., Khim. Geterotsikl.Soed., 1978, 1377.
44. M.Fujimoto, T.Sato, and K.Hata, Bull.Chem.Soc. Japan, 1967, **40**, 600.
45. N.L.Allinger, B.J.Gorden, S.Hu, and R.A.Ford, J.Org.Chem., 1967, **32**, 2272.
46. T.Sato and K.Torizuka, J.Chem.Soc., Perkin Trans. II, 1978, 1199.
47. T.Sato and K.Torizuka, J.Chem.Soc., Perkin Trans. II, 1980, 561.
48. K.Torizuka and T.Sato, Bull.Chem.Soc.Japan, 1980, **53**, 2411.
49. R.W.Griffin and R.A.Coburn, J.Org.Chem., 1967, **32**, 3956.
50. A.S.Morkovnik and O.Yu.Okhlobystin, Khim.Geterotsikl.Soed., 1980, 1011.
51. L.Eberson and F.Radner, Acta Chem.Scand., 1980, **B34**, 739.
52. L.Eberson and F.Radner, Acta Chem.Scand., 1985, **B39**, 357.
53. M.Grodowski and T.Latowski, Tetrahedron, 1974, **30**, 767.
54. M.G.Bartle, R.K.Mackie, and J.M.Tedder, Chem. Comm., 1974, 271.
55. V.A.Nefedov and L.K.Tarygina, Zhur.Org.Khim., 1976, **12**, 2012.
56. S.Ito, I.Saito, and T.Matsuura, Tetrahedron Lett., 1979, 4067.
57. L.Bin Din, O.Meth-Cohn, and N.D.A.Walshe, Tetrahedron Lett., 1979, 4783.
58. V.A.Nefedov, L.K.Tarygina, L.F.Kryuchkova, and Yu.S.Ryabokobylko, Zhur.Org.Khim., 1981, **17**, 570.
59. F.Effenberger, W.D.Stohrer, and A.Steinbach, Angew.Chem., 1969, **81**, 261.
60. C.L.Perrin, J.Amer.Chem.Soc., 1977, **99**, 5516.
61. M.L.Draper and J.H.Ridd, Chem.Comm., 1978, 445.
62. L.Eberson, L.Jonsson, and F.Radner, Acta Chem. Scand., 1978, **B32**, 749.
63. A.S.Morkovnik, E.Yu.Belinskii, and O.Yu.Okhlobystin, Zhur.Org.Khim., 1979, **15**, 1565.
64. F.Radner, Doct.Diss.Lund: Lund University, 1985, 12.
65. B.C.Gilbert, P.Hanson, R.O.C.Norman, and B.T.Sutcliffe, Chem.Comm., 1966, 161.
66. R.Gschwind and E.Haselbach, Helv.Chim.Acta, 1979, **62**, 941.
67. M.O.Delocourt and M.Rossi, J.Phys.Chem., 1982, **86**, 3233.
68. V.E.Titov, Abstract of Candidate's Thesis in Chemical Sciences, Institute of Physical Chemistry of the Academy of Sciences of the Ukrainian SSR, Kiev, 1985.
69. R.J.Schmitt, D.S.Ross, and S.E.Buttrill, J.Amer. Chem.Soc., 1981, **103**, 5265.
70. R.J.Schmitt, D.S.Ross, and S.E.Buttrill, J.Amer. Chem.Soc., 1984, **106**, 926.
71. E.Laurent, G.Raunijar, and M.Thomalla, Bull.Soc. chim.France, 1984, 78.
72. E.B.Pedersen, T.E.Petersen, K.Torssell, and S.O.Lawesson, Tetrahedron, 1973, **29**, 579.
73. N.D.Epiotis, J.Amer.Chem.Soc., 1973, **95**, 3188.
74. S.Fukuzumi and J.K.Kochi, J.Amer.Chem.Soc., 1981, **103**, 7240.
75. A.P.Rudenko, M.Ya.Zarubin, S.F.Aver'yanov, and S.F.Barsheva, Dokl.Akad.Nauk SSSR, 1979, **249**, 117.
76. C.K.Ingold, J.Chem.Soc., 1925, **127**, 513.
77. G.Cauquis, M.Genies, H.Lemaire, A.Rassatt, and J.P.Ravet, J.Chem.Phys., 1967, **47**, 4642.
78. T.Komatsu, A.Lund, and P.O.Kinell, J.Phys.Chem., 1972, **76**, 1721.
79. W.T.Dixon and D.Murphy, J.Chem.Soc., Faraday Trans.II, 1976, 1823.

80. A.V.Il'yasov, Yu.M.Kargin, and I.D.Morozova, "Spektry EPR Organicheskikh Ion-Radikalov" (The EPR Spectra of Organic Radical-Ions), Izd.Nauka, Moscow, 1980, p.125.
81. B.M.Latta and R.W.Taft, J.Amer.Chem.Soc., 1967, **89**, 5172.
82. W.Michler and S.Pattinson, Ber., 1881, **14**, 2161.
83. R.Smejtek, J.Honzl, and V.Metalova, Coll.Czech. Chem.Comm., 1965, **30**, 3875.
84. R.Herz, Ber., 1890, **23**, 2539.
85. E.Bauer and C.Haeusermann, Ber., 1898, **31**, 2987.
86. N.Donaldson, "Chemistry and Technology of Naphthalene Compounds" (Translated into Russian), Izd.GNTIKhL, Moscow, 1963, p.195.
87. P.Hedvig, "Experimental Quantum Chemistry" (Translated into Russian), Izd.Mir, Moscow, 1977, p.453.
88. O.Dimroth, Ber., 1901, **34**, 219.
89. G.Vincow, "Ion-Radicals" (Edited by E.T.Kajser and L.Kevan), Wiley, New York, 1968, pp.154, 155.
90. P.M.G.Bavin and M.J.S.Dewar, J.Chem.Soc., 1956, 164.
91. I.C.Lewis and L.S.Singer, J.Chem.Phys., 1965, **43**, 2712.
92. M.J.S.Dewar and T.Mole, J.Chem.Soc., 1956, 1441.
93. A.G.Anderson, J.A.Nelson, and J.J.Tazuma, J.Amer. Chem.Soc., 1953, **75**, 4980.
94. R.M.Dessau and S.Shih, J.Chem.Phys., 1970, **53**, 3169.
95. A.Carrington and J.D.Santos-Veiga, Mol.Phys., 1962, **5**, 285.
96. L.A.Paquette, "Principles of Modern Heterocyclic Chemistry" (Translated into Russian), Izd.Mir, Moscow, 1971.
97. M.Shiotani, Y.Nagata, M.Tasaki, J.Sohma, and T.Shida, J.Phys.Chem., 1983, **87**, 1170.
98. M.Tomita, J.Pharm.Soc.Japan, 1935, **55**, 1060.
99. S.Bodea and M.Raileanu, Studii cercetari chim., 1957, **8**, 303.
100. J.H.Ridd and E.F.Scriven, Chem.Comm., 1972, 641.
101. D.V.Banthorpe, E.D.Hughes, and D.L.H.Williams, J.Chem.Soc., 1964, 5439.
102. J.G.Boer, in "The Chemistry of Nitro- and Nitroso-Groups" (Edited by H.Feuev), Krieger, Melbourne (Translated into Russian), Izd.Mir, Moscow, 1972, Vol.1, p.211.
03. J.Blyt and A.Hofmann, Ann.Chem., 1845, **53**, 289.
04. V.V.Perekalin and A.S.Sopova, "Nepredel'nye Nitrosoedineniya" (Unsaturated Nitro-Compounds), Izd.Khimiya, Moscow–Leningrad, 1966, p.67.
05. K.Myberg, "Electrochemistry of Organic Compounds" (Translated into Russian), Izd.Mir, Moscow, 1976, p.509.
06. E.Steckhan, J.Amer.Chem.Soc., 1978, **100**, 3526.
07. R.J.Hemly, U.Dinur, V.Vaida, and M.Karplus, J.Amer.Chem.Soc., 1985, **107**, 836.
08. V.Palm, "Vvedenie v Teoreticheskuyu Organicheskuyu Khimiyu" (Introduction to Theoretical Organic Chemistry), Izd.Vys.Shkola, Moscow, 1974, p.336.
09. V.N.Kondrat'ev (Editor), "Energii Razryva Khimicheskikh Svyazei. Potentsialy Ionizatsii i Srodstvo k Elektronu" (Chemical Bond Dissociation Energies, Ionisation Potentials, and Electron Affinities), Izd. Nauka, Moscow, 1974, p.278.
110. P.Ausloos and S.G.Lias, Int.J.Chem.Kinetics, 1978, **10**, 657.
111. S.A.Benezra, M.K.Hoffman, and M.M.Bursey, J.Amer. Chem.Soc., 1970, **92**, 7501.
112. T.Takabe, K.Takenaka, K.Yamagushi, and T.Fueno, Chem.Phys.Lett., 1976, **44**, 65.
113. L.G.Gorb, I.A.Abronin, V.A.Korsunov, et al., Izv. Akad.Nauk SSSR, Ser.Khim., 1984, 1079.
114. G.Bontempelli, G.A.Mazzochin, and F.Magno, J.Electroanal.Chem., 1974, **55**, 91.
115. L.Eberson and F.Radner, Acta Chem.Scand., 1984, **38B**, 861.
116. G.Cauquis and D.Serve, Compt.rend., 1968, **267C**, 460.
117. R.G.Coombes, R.B.Moodie, and K.Schofield, J.Chem. Soc.B, 1968, 800.
118. V.A.Koptyug, O.Yu.Rodozhnikova, and A.N.Denitsa, Zhur.Org.Khim., 1983, **19**, 1129.
119. H.Suzuki and T.Ogawa, "VII IUPAC Conference on Physical Organic Chemistry, Auckland, 1984. Conference Programme and Abstracts", p.1.
120. V.Jagannadham and S.Steenken, J.Amer.Chem.Soc., 1984, **106**, 6542.
121. I.P.Beletskaja, S.P.Rykov, and A.L.Buchachenko, Org.Magn.Res.Spec.Suppl., 1973, **5**, 579.
122. A.H.Clemens, J.H.Ridd, and J.P.B.Sandall, J.Chem. Soc., Perkin Trans.II, 1984, 1659.
123. L.L.Ciaccio and R.A.Markus, J.Amer.Chem.Soc., 1962, **84**, 1838.
124. E.Hunziker, J.R.Penton, and H.Zollinger, Helv.Chim. Acta, 1971, **54**, 2043.
125. D.S.Ross, K.F.Kuhlmann, and R.Malhotra, J.Amer. Chem.Soc., 1983, **105**, 4299.
126. A.N.Detsina and V.A.Koptyug, Zhur.Org.Khim., 1972, **8**, 2215.
127. G.A.Olah, H.C.Lin, and Y.K.Mo, J.Amer.Chem.Soc., 1972, **94**, 3667.
128. L.M.Mozulenko, A.I.Rezvukhin, and V.A.Koptyug, Zhur.Org.Khim., 1972, **8**, 2531.
129. L.A.Ostashevskaya, A.N.Detsina, V.I.Mamatyuk, I.S.Isaev, and V.A.Koptyug, Zhur.Org.Khim., 1974, **10**, 2374.
130. V.F.Loktev, D.V.Korchagina, and V.G.Shubin, Izv. Sibir.Otd.Akad.Nauk SSSR, 1980(6), 86.
131. P.Helsby and J.H.Ridd, Chem.Comm., 1980, 926.
132. V.A.Koptyug, "Arenonievye Iony" (Arenium Ions), Izd.Nauka, Novosibirsk, 1983.
133. K.Kalnins, V.M.Svetlichnyi, N.G.Antonov, and M.M.Koton, Dokl.Akad.Nauk SSSR, 1978, **241**, 849.
134. K.Kalnins, M.M.Koton, N.G.Antonov, et al., Dokl. Akad.Nauk SSSR, 1979, **244**, 400.
135. K.K.Kalninsh, J.Chem.Soc., Faraday Trans.I, 1981, **77**, 227.
136. K.K.Kalninsh, Chem.Phys.Letters, 1981, **79**. 427.
137. K.Egava, N.Nakashima, N.Mataga, and C.Yamanaka, Chem.Phys.Letters, 1971, **8**, 108.
138. K.Egava, N.Nakashima, N.Mataga, and C.Yamanaka, Bull.Chem.Soc.Japan, 1971, **44**, 3287.
139. A.A.Borisenko, A.V.Nikulin, S.Wolfe, N.S.Zefirov, and N.Y.Zyk, J.Amer.Chem.Soc., 1984, **106**, 1074.
140. S.Fukuzumi, C.L.Wong, and J.K.Kochi, J.Amer.Chem. Soc., 1980, **102**, 2928.
141. G.A.Olah, B.G.B.Gupta, and S.C.Narang, J.Amer. Chem.Soc., 1979, **101**, 5317.
142. A.S.Morkovnik, Khim.Geterotsikl.Soed., 1985, 274.
143. C.A.Bunton, E.G.Hughes, C.K.Ingold, D.I.H.Jacobs, M.H.Jones, G.J.Minkoff, and R.I.Reed, J.Chem.Soc., 1950, 2628.
144. F.Al-Omran and J.H.Ridd, J.Chem.Soc., Perkin Trans.II, 1981, 518.
145. F.Al-Omran and J.H.Ridd, J.Chem.Soc., Perkin Trans.II, 1983, 1185.
146. B.C.Challis and A.J.Lawson, J.Chem.Soc.B, 1971, 770.

147. D.S.Ross, G.P.Hum, and W.G.Blucher, Chem.Comm., 1980, 532.
148. D.S.Ross, K.D.Moran, and R.Malhotra, J.Org. Chem., 1983, **48**, 2118.
149. L.Main, R.B.Moodie, and K.Schofield, Chem.Comm., 1982, 48.
150. B.K.Bandlish and H.J.Shine, J.Org.Chem., 1977, **42**, 561.
151. A.S.Morkovnik, N.M.Dobaeva, and O.Yu.Okhlobystin, Khim.Geterotsikl.Soed., 1981, 845.
152. A.S.Morkovnik, N.M.Dobaeva, M.M.Levkovich, et al., "Tezisy Dokladov VI Vsesoyuznogo Simpoziuma po Kompleksam s Perenoson Zaryada i Ion-Radikal'nym Solyam" (Abstracts of Reports at the VIth All-Union Symposium on Charge-Transfer Complexes and Radical-Ion Salts), Chernogolovka, 1984, p.157.
153. A.S.Morkovnik and O.Yu.Okhlobystin, Zhur.Obshch. Khim., 1985, **55**, 692.
154. Z.J.Allan, J.Podstata, D.Snobl, and J.Jarkovski, Coll.Czech.Chem.Comm., 1967, **32**, 1449.
155. J.M.Tedder, in "The Chemistry of Synthetic Dyes" (Edited by K.Venkataraman), Academic Press, London (Translated into Russian), Izd.Khimiya, Leningrad, 1974, Vol.3, p.1881.
156. T.J.Richardson and N.Bartlett, Chem.Comm., 1974, 427.
157. S.J.Lias and P.Ausloos, J.Amer.Chem.Soc., 1977, **99**, 4831.
158. W.D.Reents and B.S.Freiser, J.Amer.Chem.Soc., 1980, **102**, 271.
159. T.A.Turney and G.A.Wright, J.Chem.Soc., 1958, 2415.
160. V.N.Kondrat'ev (Editor), "Energii Razryva Khimicheskikh Svyazei. Potentsialy Ionizatsii i Srodstvo k Elektronu" (Chemical Bond Dissociation Energies, Ionisation Potentials, and Electron Affinities), Izd. Nauka, Moscow, 1974, p.327.
161. V.M.Bernikov and N.M.Bazhin, Zhur.Fiz.Khim., 1970, **44**, 712 [Russ.J.Phys.Chem., 1970(3)].
162. A.S.Morkovnik and O.Yu.Okhlobystin, "Novoe v Khimii Azotistykh Geterotsiklov" (Advances in the Chemistry of Nitrogen-Containing Heterocycles), Izd. Zinatne, Riga, 1979, Vol.2, p.190.
163. K.Singer and P.A.Vamplev, J.Chem.Soc., 1956, 3971.
164. G.Schmid and G.Kirchel, Ber., 1964, **68**, 677.
165. A.S.Morkovnik, N.M.Dobaeva, and O.Yu.Okhlobystin, "Tezisy Dokladov III Vsesoyuznogo Simpoziuma po Organicheskomu Sintezu" (Abstracts of Reports at the IIIrd All-Union Symposium on Organic Synthesis), Institute of Organic Chemistry, USSR Academy of Sciences, Moscow, 1981, p.5.
166. E.Abel and H.Schmidt, Z.phys.Chem., 1928, **134B**, 279.
167. G.Catra and R.L.Pigford, Ind.and Eng.Chem. Fundam., 329.
168. K.E.Friend and W.E.Ohnesorge, J.Org.Chem., 1963, **28**, 2435.
169. V.D.Parker, Acta Chem.Scand., 1970, **24**, 2757.
170. B.Rindone and C.Scolastico, J.Chem.Soc.B, 1971, 2238.
171. W.A.Prior, G.J.Gleicher, J.P.Cosgrove, and D.F.Church, J.Org.Chem., 1984, **49**, 5189.
172. I.R.Epstein, K.Kustin, and L.J.Warschaw, J.Amer. Chem.Soc., 1980, **102**, 3751.
173. B.C.Challis, R.J.Higgins, and A.J.Lawson, J.Chem. Soc., Perkin Trans.II, 1972, 1831.
174. J.H.Ridd and J.P.B.Sandall, Chem.Comm., 1981, 402.
175. A.H.Clemens, J.H.Ridd, and J.P.B.Sandall, Chem. Comm., 1983, 343.
176. A.H.Clemens, J.H.Ridd, and J.P.B.Sandall, J.Chem. Soc., Perkin Trans.II, 1984, 1667.
177. A.H.Clemens, J.H.Ridd, and J.P.B.Sandall, J.Chem. Soc., Perkin Trans.II, 1985, 1227.
178. L.Eberson and F.Radner, Acta Chem.Scand., 1985, **B39**, 343.
179. B.Milligan, J.Org.Chem., 1983, **48**, 1495.
180. K.V.Altukhov and V.V.Perekalin, Uspekhi Khim., 1976, **45**, 2050 [Russ.Chem.Rev., 1976(11)].
181. V.A.Petrosyan, V.I.Slovetskii, S.G.Mairanovskii, and A.A.Fainzil'berg, Elektrokhimiya, 1970, **6**, 1595.
182. V.M.Berdnikov, L.A.Terent'eva, and O.S.Zhuravleva, Izv.Akad.Nauk SSSR, Ser.Khim., 1976, 2655.
183. S.A.Shevelev, R.V.Kolesnikov, and I.P.Beletskaya, Zhur.Org.Khim.. 1974, **9**, 1793.
184. S.A.Shevelev, R.V.Kolesnikov, A.A.Fainzil'berg, and I.P.Beletskaya, Izv.Akad.Nauk SSSR, Ser.Khim., 1975, 1368.
185. J.N.Chaudhuri, J.Chem.Soc., 1959, 3085.
186. V.E.Kholmogorov and V.A.Gorodyskii, Zhur.Fiz. Khim., 1972, **46**, 63 [Russ.J.Phys.Chem., 1972(1)].
187. D.H.Iles and A.Ledwith, Chem.Comm., 1969, 364.
188. E.M.Maksyutov, I.A.Leenson, G.B.Sergeev, and V.I.Slovetskii, Vestnik Moskov.Gos.Univ., Ser.Khim., 1980, 21, 262.
189. D.W.Amos, D.A.Baines, and G.W.Flewett, Tetrahedron Lett., 1973, 3191.
190. R.J.Coombes and L.W.Russell, J.Chem.Soc., Perkin Trans.I, 1974, 1751.
191. R.J.Coombes and L.W.Russell, J.Chem.Soc., Perkin Trans.II, 1974, 830.
192. G.I.Nikishin, E.P.Kaplan, and N.I.Kapustina, Izv. Akad.Nauk SSSR, 1975, 1434.
193. B.O.Field and C.J.Hardi, J.Chem.Soc., 1963, 5278.
194. B.O.Field and C.J.Hardi, J.Chem.Soc., 1964, 4428.
195. R.J.Fereday and N.Logan, Chem.Comm., 1968, 271.
196. C.C.Addison and B.J.Hathaway, J.Chem.Soc., 1958, 3099.
197. S.Dinckturck and J.H.Ridd, J.Chem.Soc., Perkin Trans.II, 1982, 965.
198. S.Dinckturck and J.H.Ridd, J.Chem.Soc., Perkin Trans.II, 1982, 961.
199. A.S.Morkovnik and O.Yu.Okhlobystin, Khim.Geterotsikl.Soed., 1981, 123.
200. M.E.Kurz and W.G.Hage, J.Org.Chem., 1977, **42**, 4080.
201. L.Eberson, "Organic Electrochemistry" (Translated into Russian), Izd.Mir, Moscow, 1976, p.560.
202. H.J.Shine and L.R.Shade, J.Heterocycl.Chem., 1974, 11, 139.
203. J.E.Pemberton and J.E.Evans, J.Phys.Chem., 1979, **83**, 2696.
204. R.O.C.Norman, W.J.E.Parr, and C.B.Thomas, J.Chem.Soc., Perkin Trans.I, 1974, 369.
205. I.V.Kozhevnikov, Dokl.Akad.Nauk SSSR, 1980, 252, 915.
206. W.N.White, J.R.Klink, D.Lazdins, et al., J.Amer. Chem.Soc., 1961, **83**, 2024.
207. W.N.White and H.S.White, J.Org.Chem., 1970, 35, 1803.
208. W.N.White and J.T.Goulden, J.Org.Chem., 1970, 35, 2759.
209. W.N.White and H.S.White, J.Org.Chem., 1976, 41, 3166.
210. J.H.Ridd and J.P.B.Sandall, Chem.Comm., 1982, 261.

211. H.J.Shine, J.Zygmunt, M.L.Brownawell, and J.S.Filippo, J.Amer.Chem.Soc., 1984, **106**, 3610.
212. P.Helsby and J.H.Ridd, Chem.Comm., 1981, 825.
213. Z.V.Todres, "Ion-Radikaly v Organicheskom Sinteze" (Radical-Ions in Organic Synthesis), Izd.Khimiya, Moscow, 1986, p.110.
214. Z.V.Todres, Tetrahedron, 1985, **41**, 2771.
215. A.S.Morkovnik, M.M.Levkovich, V.D.Stebletsova, et al., Zhur.Obshch.Khim., 1987, **57**, 1663.
216. A.Kurfurst and J.Kuthan, Coll.Czech.Chem.Comm., 1984, **49**, 2620.
217. A.Boughriet, J.-C.Fischer, M.Wartel, and C.Bremard, Nouv.J.Chim., 1985, **9**, 651.
218. L.G.Forni, V.O.Mora-Arellano, J.E.Packer, and R.L.Willson, J.Chem.Soc., Perkin Trans.II, 1986, 1.
219. A.J.Frank and M.Gratzel, Inorg.Chem., 1982, 21, 3834.

Institute of Physical
and Organic Chemistry,
Suslov Rostov State
University