Russian Chemical Reviews **70** (3) 211 – 230 (2001) © 2001 Russian Academy of Sciences and Turpion Ltd

DOI 10.1070/RC2001v070n03ABEH000634

Nitrosonium complexes of organic compounds. Structure and reactivity

G I Borodkin, V G Shubin

Contents

I.	Introduction	211
II.	Complexes of the nitrosonium ion with alkanes	211
III.	Complexes of the nitrosonium ion with alkenes	212
IV.	Nitrosonium complexes of aromatic compounds	214
V.	Complexes of the nitrosonium ion with nitrogen-containing organic compounds	223
VI.	Complexes of the nitrosonium ion with organic compounds containing Group VI elements	225
VII.	Complexes of the nitrosonium ion with halogen-containing organic compounds	228

Abstract. Data on the structures and reactivities of nitrosonium complexes of organic compounds are systematised and generalised. The characteristic features of the electronic structure of the NO^+ cation are responsible for a wide structural variety of nitrosonium complexes. Reactions of nitrosonium complexes are described. The bibliography includes 172 references.

I. Introduction

Nitrosonium complexes of organic compounds have been extensively studied over many years. The continuing interest in these complexes stems from the fact that they are intermediates in a series of reactions, including nitrosation of aromatic compounds,[1] nitrosohalogenation of alkenes,[2–4] *etc*.[5] Recently, interest in these complexes has increased due to the discovery of the unique role of the NO molecule in biochemical processes.[6–15] It is assumed that the nitrosonium cation and some molecules generating the nitrosonium ion are involved in processes of neurotoxic and neuroprotective actions of nitric oxide[16,17] (*cf*. Refs 18–20)† and participate in cross-linking of DNA.[21,22]

Investigations of the structures and reactivities of nitrosonium complexes are essential to the understanding of the role of the NO^+ cation in various chemical processes (from ionospheric[23,24] to biochemical[9,16–19]) giving rise to different classes of organic compounds.

In the present review, the data on the structures and reactivities of nitrosonium complexes published over the last 10–15 years are analysed and systematised. The results of earlier studies are cited if they are necessary for an understanding of the problem and for elucidation of new trends in this area of exploration.

† Hereinafter, the reader is referred to studies, which are either indirectly associated with the problem under consideration or even contradictory.

G I Borodkin, V G Shubin N N Vorozhtsov Novosibirsk Institute of Organic Chemistry, Siberian Branch of the Russian Academy of Sciences, prosp. Akad. Lavrent'eva 9, 630090 Novosibirsk, Russian Federation.
Fax (7-383) 234 47 52. Tel. (7-383) 234 43 86.
E-mail: gibor@nioch.nsc.ru (G I Borodkin).
Tel. (7-383) 234 26 51. E-mail: vshubin@nioch.nsc.ru (V G Shubin)

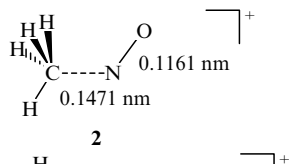
Received 10 November 2000
Uspekhi Khimii **70** (3) 241 – 261 (2001); translated by T N Safonova

II. Complexes of the nitrosonium ion with alkanes

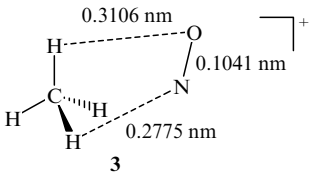
Electrophilic substitution in the aliphatic series of compounds lies at the basis of one of the procedures for the functionalisation of alkanes.[25–27] Weak electrophiles, in particular NO^+, can be involved in electrophilic aliphatic substitution reactions along with strong electrophiles, such as H^+ and Alk^+. Nitrosonium salts react with adamantane in the presence of HF, oxygen or nitriles to form 1-fluoroadamantane,[28] 1-nitroadamantane[29] or *N*-(1-adamantyl)amides,[30] respectively. Generally, it is assumed that the attack of the electrophile E^+ in electrophilic aliphatic substitution reactions occurs at the C–H bond to give intermediates of the type **1** characterised by the two-electron three-centre mode of bonding of the E, H and C atoms (3X-2e-intermediates)[25–27] (*cf*. Ref. 31).

$$HCR_3 + E^+ \longrightarrow \underset{\mathbf{1}}{\overset{E^+}{H\cdots CR_3}} \longrightarrow CR_3E + H^+$$

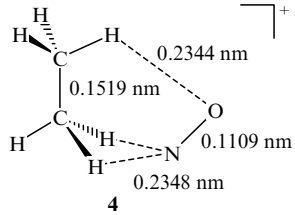
According to high-level *ab initio* calculations for the reactions of the NO^+ cation with methane and ethane,[32,33] the mechanism of the reactions of the nitrosonium cation with alkanes might differ from that described above. Thus, the NO^+ cation attacks the methane molecule at the carbon atom to form complex **2** whose precursor is unstable complex **3** [$\Delta H_0 = -15.5$ kJ mol^{-1}, where ΔH_0 is the relative energy of the complex taking into account the zero-point energy; the results of calculations by the MP4SDTQ/6-31 + G(dp)/MP2/6-31 + G(dp) + ZPVE//MP2/6-31 + G(dp) method]. An alternative path involving the attack of the NO^+ cation at the C–H bond is less favourable (by 60.2 kJ mol^{-1}).



2



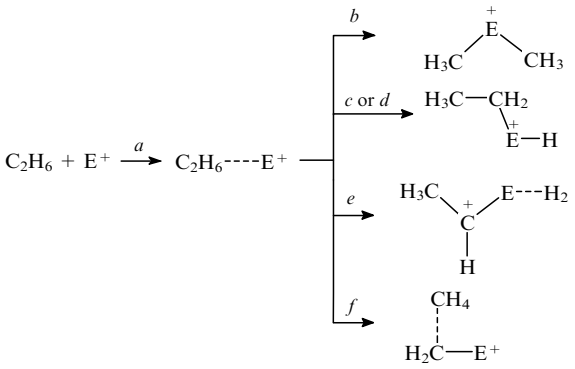
3



4

Analogously, unstable complex **4** {$\Delta H_0 = -16.7$ kJ mol^{-1}; calculations by the CISD + Q/TZP + //MP2/6-31G(dp) + ZPVE[MP2/6-31G(d)] method} is initially formed in the reaction with ethane. In the latter complex, the NO^+ cation is bound to the ethane molecules *via* polarisation and Coulomb interactions.[33] Subsequent conversions of this complex are shown in Scheme 1.

Scheme 1



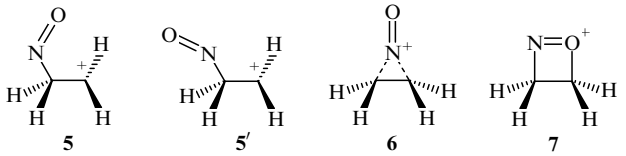
(*a*) $\Delta H_0 = -17.2$ kJ mol^{-1}; (*b*) insertion of E^+ at the C–C bond; $\Delta H_0 = -118.8$ kJ mol^{-1}; (*c*) insertion of E^+ at the C–H bond, $\Delta H_0 = -84.5$ kJ mol^{-1}; (*d*) elimination of H^-, addition of EH, $\Delta H_0 = -84.5$ kJ mol^{-1}; (*e*) elimination of H_2, $\Delta H_0 = 119.2$ kJ mol^{-1}; (*f*) elimination of CH_4, $\Delta H_0 = 39.7$ kJ mol^{-1}.

Although the attack of the NO^+ cation at the C–C bond is thermodynamically favourable (see Scheme 1), Schreiner *et al.*[33] believed that the attack on the C (to form a complex of the type **2**) and H atoms is kinetically more favourable. Elimination of the H_2 molecule is also unlikely because this path is thermodynamically unfavourable ($\Delta H_0 = 119.2$ kJ mol^{-1}). Attempts to isolate the transition states in these reactions failed. The activation barriers to elimination of methane and the hydride ion giving rise to nirosomethane and nirosoethane, respectively, have similar values (140.2 and 130.1 kJ mol^{-1}, respectively).

III. Complexes of the nitrosonium ion with alkenes

In a series of investigations, alkene–NO^+ complexes were proposed as intermediates of reactions of alkenes with nitrosyl halides[2–4] and $[NO]^+X^-$ salts (see Refs 34–37). These reactions are of importance in the synthesis of halonitroso- and halonitroorganic,[1–4,38] N,O-heterocyclic[34–36,39] and some other organic compounds.[37,40–42]

The energy profiles of fluoronitrosation of ethylenes were calculated by the MINDO/3 and UMINDO/3 quantum-chemical methods.[43] The facts that the NO^+ cation approaches the ethylene molecule at an angle to the symmetry plane of the latter and attacks the carbon atom to form σ-complex **5** are attributed to a strong $\pi_\sigma - \pi_\sigma$ interaction between the unoccupied e(π*)-MO of the NO^+ cation and HOMO of ethylene.



According to the results of MINDO/3 calculations, the isomeric form **5′** is less favourable than the structure **5** ($\Delta\Delta H_f = 22.2$ kJ mol^{-1}, where ΔH_f is the enthalpy of complex formation). The open cation **5** is rearranged into isomeric cyclic structures **6** and **7**, the activation energies (E_a) of these rearrangements being low ($E_a = 5.0$ and 14.2 kJ mol^{-1}, respectively). Among the structures **5**–**7**, the π-complex **6** is the most stable.

Ab initio calculations (the STO-3G basis set) predicted that the structure **7** should be the most stable.[43] Higher-level *ab initio* quantum-chemical calculations (MP4/6-31G + D) also provided evidence for higher stability of the structure **7** (Table 1).[44] In addition to the π-complex **6** in which the NO group is located in proximity to the ethylene fragment [the distance from the N atom to the C–C bond (*d*) is 0.1272 nm], more favourable (within the framework of the MP4 method) 'loose' π-complex **9** was found. In the latter, the distance *d* is substantially larger (0.1978 nm) and the NO group is located at an angle to the plane passing through the C, C and N atoms (Fig. 1, see Table 1).

Table 1. Relative energies (E_{rel} /kJ mol^{-1}) of the structures **7**–**10** obtained by *ab initio* quantum-chemical calculations.[44]

Structure	Basis set	E_{rel} [a] calculated by the method				
		HF	MP2	MP3	MP4	CCD + ST(4)
7	STO-3G	−335.6	–	–	–	–
	6-31G	−77.4	76.6	−36.8	43.1	–
	6-31G + D	−75.3	−16.3	−75.7	−33.1	–
8	STO-3G	−223.8	–	–	–	–
	6-31G	−89.1	31.0	−79.5	17.6	5.0
	6-31G + D	−35.1	−15.9	−60.7	−11.7	−13.8
9	STO-3G	−132.6	–	–	–	–
	6-31G	−65.7	−10.5	−76.1	−31.8	−38.1
	6-31G + D	−30.1	−41.4	−61.9	−49.4	−50.2
10	STO-3G	−139.7	–	–	–	–
	6-31G	−49.4	59.4	−27.2	22.2	13.4
	6-31G + D	5.4	33.1	−2.9	7.9	6.7

[a] The total energy of the C_2H_4 molecule and the NO^+ cation was taken equal to zero.

The σ-complex **10** is substantially less stable than the π-complexes **8** and **9** (see Table 1, Fig. 1). The C–N bond in the cation **10** is unusually long, which indicates that the C and N atoms are weakly bound together[44] (*cf.* Refs 37 and 43).

The structural and energy characteristics of the nitrosonium complexes with cyclobutadiene were calculated by the MINDO/3 and *ab initio* methods (the STO-3G basis set).[45] Qualitative analysis of orbital interactions revealed five structures with attractive interactions of the $\pi_\sigma - \pi_\sigma (p_\sigma - \pi_\sigma)$ type between the NO^+ cation and the ring. In the complexes **11** and **12**, the nitroso group is located parallel to the plane of the carbon ring above its centre and above one of the double bonds, respectively.

In the structures **13**–**15**, the NO group is perpendicular to the plane of the ring. Interactions between the orbitals of the nitroso group and the π orbitals of one of the double bonds occur in the isomers **13** and **15**, whereas interactions between the orbitals of the nitroso group and all π orbitals of the ring take place in the pyramidal structure **14**. The energy characteristics of the cations **11**–**13**, **15**, **17** and **18** are given in Table 2. According to calculations by the MINDO/3 method, the azapyrylium cation **18** is the most stable one in the above-mentioned series.

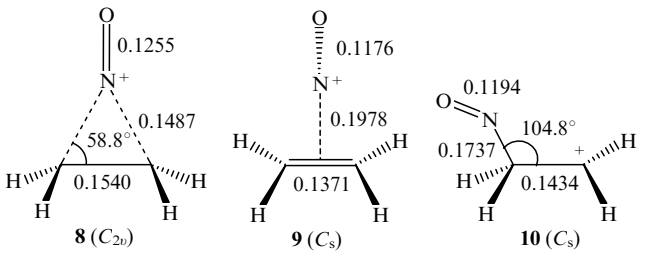
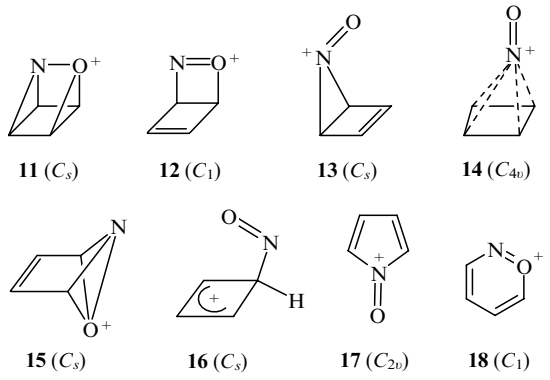


Figure 1. Geometric parameters of the π-complexes **8** and **9** and the σ-complex **10** obtained by *ab initio* calculations (the STO-3G basis set).[44] The bond lengths are expressed in nm; the symmetry is given in parentheses.

Table 2. Enthalpies of formation (ΔH_f), total energies (E_{tot}) and relative energies (E_{rel}) of the structures **11**–**13**, **15**, **17** and **18**.[45]

Parameter	**11**		**12**		**13**		**15**	**17**	**18**
	MINDO/3	STO-3G	MINDO/3	STO-3G	MINDO/3	STO-3G	MINDO/3		
ΔH_f /kJ mol^{-1}	1036.0	–	1016.3	–	1044.7	–	885.8	931.4	681.6
E_{tot} /a.u.[a]	–	−279.1292	–	−279.1439	–	−279.0593	–	–	–
E_{rel} /kJ mol^{-1}	354.4	38.6	334.7	0	363.1	222.1	204.2	249.8	0

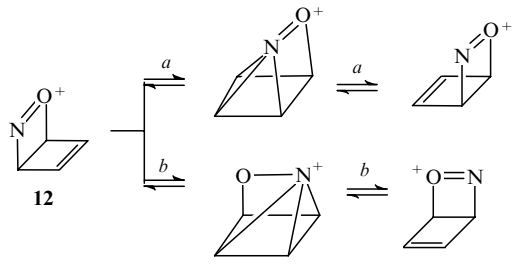
[a] 1 a.u. = 2625.5 kJ mol^{-1}.



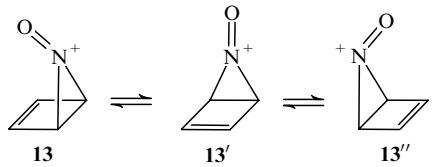
Ab initio calculations (the STO-3G basis set) for the structures **11**–**13** predicted the higher stability of the cation **12**. In the case of the pyramidal structure **14**, no minimum was found on the potential energy surface (PES).‡ The conversion of this structure into the structure **13** is barrierless, the latter being the only η^n structure ($n = 1-4$) corresponding to a local minimum. There is also no minimum on the potential energy surface corresponding to the σ-complex **16**. Minkin *et al.*[45] believe that attempts to generate the nitrosocyclobutenyl cation in the gas phase or in a weakly solvating solvent will fail.

Calculations by the MINDO/3 method for the structure **12** predicted that the nitroso group can either migrate parallel to the plane of the cyclobutadiene ring (Scheme 2, path *a*) or rotate about the C–O bond (Scheme 2, path *b*).[45]

Scheme 2



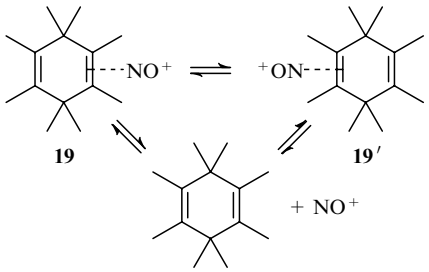
For the η^2-isomer **13**, the rotational-type rearrangement **13** ⇋ **13′** ⇋ **13″** with the low energy barrier (E_a = 46.9 kJ mol^{-1}) involving cation **16** as the transition state was revealed.[45]



‡ *Ab initio* calculations taking into account the electron correlation (MP2/6-31G*+ZPE) also demonstrated that the structure **14** does not correspond to the minimum on the PES.[46]

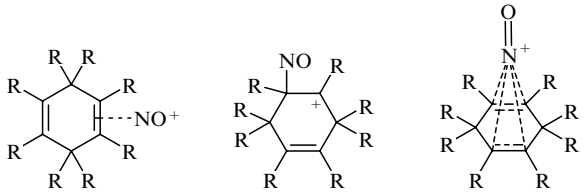
It should be noted that the above-considered topomerisation reactions of the structures **12** (see Scheme 2) and **13** are, apparently, of only theoretical interest because these complexes are kinetically unstable and are converted into the structures **18** and **17**, respectively, with low energy barriers (E_a = 14.2 and 16.7 kJ mol^{-1}, respectively).[45]

Until recently, experimental data on π-complexes of alkenes with the nitrosonium cation were lacking in the literature. Attempts to synthesise complexes of this type by reactions of $[NO]^+[BF_4]^-$ with ethylene or 2,3-dimethylbut-2-ene failed. In the former case, the reaction did not proceed, whereas the latter reaction afforded exclusively polymeric products.[47] Olah *et al.*[47] believed that the reaction of $[NO]^+[BF_4]^-$ with adamantylideneadamantane gave rise to either a dynamical σ-complex or a π-complex. However, the authors failed to choose between these complexes. The first reliable data on the synthesis of an alkene–NO^+ complex were obtained in a study by Borodkin and coworkers.[48] According to the results of ^{1}H, ^{13}C and ^{27}Al NMR spectroscopy using the isotope perturbation method, the complex of 1,2,3,3,4,5,6,6-octamethylcyclohexa-1,4-diene with the NO^+ cation is a η^2-type π-complex (structure **19**).[48,49] It appeared that this complex underwent degenerate π,π-rearrangement **19** ⇋ **19′** (in the $SO_2-SO_2ClF-CD_2Cl_2$ system), rapid within the NMR time scale even at low temperature (−80 to −90 °C), the rate of intramolecular transfer of the NO^+ group being higher than the rate of intermolecular transfer.



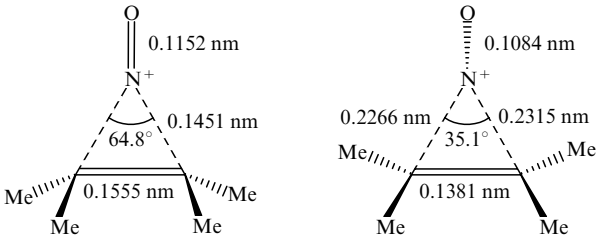
The rate of the intermolecular rearrangement increases on going from the $SO_2-SO_2ClF-CD_2Cl_2$ system to the $SO_2-CD_2Cl_2$ system.[48,49]

The results of quantum-chemical calculations for the nitrosonium complexes with cyclohexa-1,4-diene and 1,2,3,3,4,5,6,6-octamethylcyclohexa-1,4-diene by the MINDO/3 and MNDO/PM3 methods indicate that η^2-type π-complexes (**20** and **21**) are more stable than the corresponding σ-complexes (**22** and **23**) and η^4-type π-complexes (**24** and **25**)[48,49] through which intramolecular transfer of the nitroso group apparently proceeds.



R = H (**20**, **22**, **24**), Me (**21**, **23**, **25**).

As mentioned above, *ab initio* calculations provided evidence for the existence of two types of ethylene complexes with the NO^+ cation (**8** and **9**). These complexes differ in geometry and, primarily, in the distance between the nitrogen atom and the C=C bond (d = 0.1272 and 0.1978 nm, respectively).[44] The structure of the nitrosonium complex with 2,3-dimethylbut-2-ene was analysed in detail by ^1H and ^{13}C NMR spectroscopy using the isotope perturbation method and by *ab initio* quantum-chemical (6-31G* basis set) and IGLO calculations.[50] As in the case of the ethylene–NO^+ isomers, the calculations predicted the existence of two types of complexes characterised by the symmetry C_{2v} (**26**) and the approximate symmetry C_s (**27**). In these complexes, the distances from the N atom to the C=C bond are 0.1225 and 0.2183 nm, respectively.

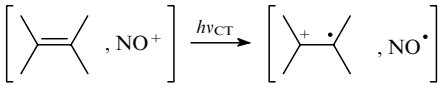


26 (C_{2v}) **27** ($\sim C_s$)

In the complexes **26** and **27**, the energies of binding of the nitrosonium cation with 2,3-dimethylbut-2-ene are 93.7 and 117.6 kJ mol^{-1}, respectively, which is indicative of higher stability of the complex **27**. The experimental chemical shifts of the C(2) and C(3) atoms (190.2 ppm) are substantially closer to those calculated by the IGLO(DZ) method for the complex **27** (δ_C 183.4 and 189.8, respectively) than to those for the complex **26** (δ_C 67.2). The equivalence of the C(2) and C(3) atoms and the equivalence of the carbon atoms of the methyl groups observed in the ^{13}C NMR spectrum of the complex **27** were attributed either to the inversion of the nitrogen atom or to the rotation of the NO group about the axis passing through the nitrogen atom perpendicular to the C(2)–C(3) bond as well as to the high rate of migration of this group.[50]

Complexes of different alkenes with the $[NO]^+[BF_4]^-$ and $[NO]^+[PF_6]^-$ salts and with other sources of the nitrosonium cation ($RONO-CF_3CO_2H$, $NOCl-CF_3CO_2H$ and $N_2O_4-SbF_5$) were investigated.[51] At low temperature, the electronic spectra of 2,3-dimethylbut-2-ene, 2,3,4-trimethylpent-2-ene and adamantylideneadamantane have charge-transfer bands. The reactions of other alkenes, such as 2,5-dimethylhex-2-ene, 2,4,4-trimethylpent-2-ene, 1-methylcyclohexene, cyclohexene, 2,3,3-trimethylbut-1-ene, norbornene, 3,3-dimethylbut-1-ene and hex-1-ene, with the above-mentioned salts either afforded slightly coloured solutions or did not give coloured solutions corresponding to the formation of charge-transfer complexes at all. These differences in the behaviour of alkenes containing the completely substituted C=C bond and those with the partially substituted C=C bond were attributed to the difference in the oxidation potentials (E_{ox}) of these alkenes.[51] Thus the oxidation potentials of 2,3-dimethylbut-2-ene and 2,3,4-trimethylpent-2-ene (E_{ox} = 1.6 V) are substantially smaller than those of 2-methylbut-2-ene and but-2-ene ($E_{ox} \approx$ 2.0 and 2.4 V, respectively). The thermal and photochemical behaviour of the alkene–NO^+ complexes is explained by the formation of charge-transfer complexes.

The photochemical activation of these complexes leads to generation of the corresponding radical cations. Thus irradiation of 2,3-dimethylbut-2-ene and N_2O_4 in a matrix at the frequency corresponding to the charge-transfer band (ν_{CT}) at 75 K afforded a pair of the type **28**.

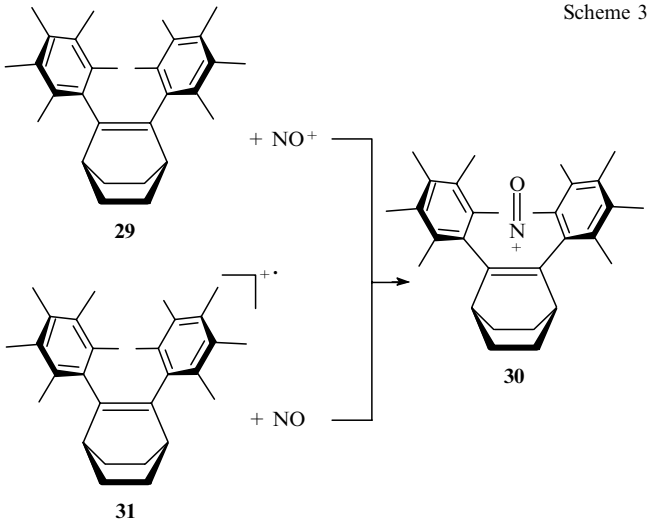


28

The subsequent reaction of the radical cation of 2,3-dimethylbut-2-ene with nitric oxide gave rise to the 1-nitroso-2,3-dimethylbut-2-yl cation, which reacted with the NO_3^- anion to form nitrosonitrate.[51,52]

The reaction of 1,2-bis(pentamethylphenyl)bicyclo[2.2.2]oct-2-ene (**29**) with the nitrosonium cation in CH_2Cl_2 at 25 °C afforded π-complex **30**. The characteristic feature of the latter complex is the fact that the NO group in this complex can interact with both the double bond and the aromatic rings (Scheme 3).[53]

Scheme 3

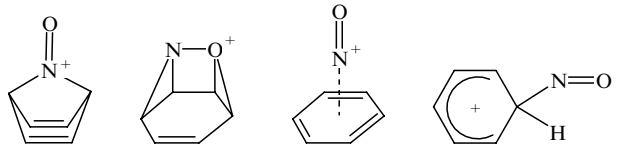


Electrochemical oxidation of the alkene **29** gave rise to the corresponding radical cation **31** whose reaction with gaseous nitric oxide afforded the same π-complex **30**[53] (*cf.* Ref. 54). X-Ray diffraction analysis of the π-complex **30** (with the $SbCl_6^-$ counterion) revealed the presence of noncovalent bonding of the NO^+ cation with the aromatic rings (the average distance to the plane of the rings is ~0.25 nm) and with the double bond, the positive charge being primarily localised at the aromatic and alkene carbon atoms, respectively.[53] The C(1)=C(2) bond length in the complex **30** (0.137 nm) is larger than that in the precursor **29** (0.133 nm) and is virtually identical to the above-mentioned C=C bond lengths in the complexes **9** and **27** determined by *ab initio* calculations. The strong bond between the NO^+ group and the unsaturated system in the complex **30** is consistent with its high formation constant ($> 3 \times 10^6$ litre mol^{-1}).[53]

IV. Nitrosonium complexes of aromatic compounds

Nitrosonium complexes of monocyclic aromatic compounds have been investigated in sufficient detail.[44,55–90] These complexes attract the attention of organic chemists primarily because they are analogues of intermediates of such important reactions as diazotisation, C-nitrosation and nitration proceeding through nitrosation of aromatic compounds[1,90–95] (*cf.* Ref. 96). In addition, it is known that the NO^+ cation catalyses bromination of aniline derivatives[97] and proton exchange in the *N*,*N*-dimethylanilinium ion,[98] which was assigned to the formation of the corresponding arene–NO^+ complexes.

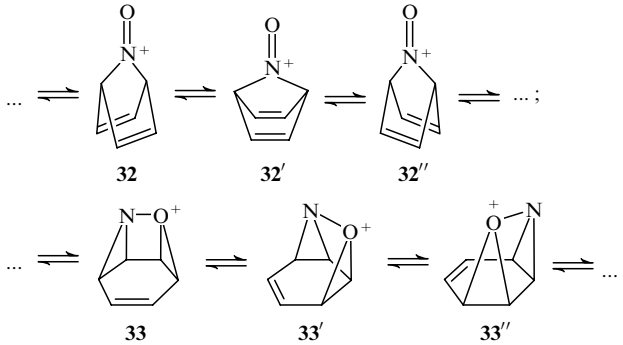
The nitrosation of benzene was investigated by quantum-chemical methods.[70] Thus, the pathway of electrophilic replacement of the hydrogen atom in the benzene ring by the NO^+ cation was calculated by the MINDO/3 method. Initially, the electron is transferred from the frontier orbital of the benzene molecule to the π* orbital of the nitrosonium cation to form π-complexes **32** and **33**. The enthalpies of their formation are 1017.1 and 959.0 kJ mol^{-1}, respectively.



32 (C_{2v}) **33** (C_1) **34** (C_{6v}) **35** (C_s)

According to the rule of electron counting for pyramidal structures,[99–101] the π-complex **34** with the symmetry C_{6v} is unstable (ΔH_f = 1031.8 kJ mol^{-1}) and corresponds to a peak top on the potential energy surface. A shallow minimum on the PES (8.4 kJ mol^{-1}) corresponds to the structure of σ-complex **35** (ΔH_f = 928.8 kJ mol^{-1}), which indicates that it is not detectable experimentally.

Calculations for the π-complexes **32** and **33** provided evidence for the occurrence of a sixfold-degenerate rearrangement with a low energy barrier (E_a < 12.6 kJ mol^{-1}) caused by 'switching' of the C–N bond in the complex **32** and migration of the nitroso group over the plane of the ring in the structure **33**:

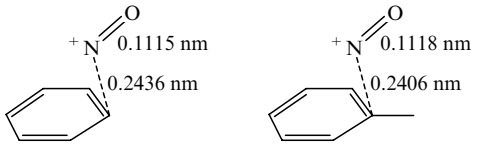


32 **32′** **32″**

33 **33′** **33″**

The $\Delta\Delta H_f$ value (relative to the $C_6H_6-NO^+$ system) found by higher-level quantum-chemical calculations (*ab initio*, MP2/6-31G+D)[44] for the centrosymmetrical structure **34** is −189.1 kJ mol^{-1}, which is close to the experimental value for the gas phase (−172±21 kJ mol^{-1}).[44,64] The corresponding σ-complex is substantially less stable ($\Delta\Delta H_f$ = −23.4 kJ mol^{-1}).

Ab initio B3LYP/6-31G(d) calculations revealed stable π-complex **36** with the symmetry C_1. The energy of its formation from benzene and the NO^+ cation is −220.5 kJ mol^{-1}.[89] In addition, the calculations gave local minima for the π-complexes **32** and **33** whose relative energies are 163 and 201 kJ mol^{-1}, respectively, smaller than that in the case of the π-complex **36**.



36 **37**

According to the results of quantum-chemical calculations, the π-complex of toluene with the NO^+ cation (**37**) is more stable than the π-complex **36** (ΔE_{rel} = 17.6 kJ mol^{-1}). The stretching vibration frequency of the NO group calculated for the complex **37** (2087 cm^{-1}) is smaller than that for the complex **36** (2110 cm^{-1}), which is indicative of a higher degree of electron density transfer from the aromatic ring to the NO group in the cation of the complex **37**.[89]

The first experimental data on the formation of $ArH-NO^+$ π-complexes were obtained by electronic spectroscopy of nitrosonium complexes of benzene and its derivatives.[58,59] Shortly thereafter, π-complexes of the NO^+ cation with benzene derivatives were investigated by Allan *et al.*[60,61] More recently, NMR spectroscopy along with electronic and IR spectroscopy were employed for studying cationic π-complexes. The available spectral data for the nitrosonium π-complexes of benzene and its derivatives are summarised in Tables 3–5. The formation of π-complexes leads to characteristic changes, in particular, to downfield shifts of the signals in the ^1H and ^{13}C NMR spectra (see Tables 3 and 4, respectively), to the appearance of charge-transfer bands in the electronic spectra and to a decrease in the stretching vibration frequency of the NO group in the complexes compared to those in $[NO]^+X^-$ salts (see Table 5). Apparently, all the above-mentioned changes are caused by the electron density transfer from the aromatic moiety of the complex to the nitroso group.

Table 3. ^1H NMR spectral data for the π-complexes of benzene and its derivatives with the nitrosonium cation (the molar ratio $ArH:[NO]^+X^- = 1:1$).

Compound	Salt	Solvent	Chemical shifts (δ_H) [a]		Ref.
			CH_3	H_{arom}	
Benzene	$NOAlCl_4$	SO_2		8.03 (0.62)	72
	$NOGaCl_4$	SO_2		7.75 (0.34)	72
	$NOHSO_4$	H_2SO_4		7.89	64
	see [b]	see [c]		7.49 (0.11)	78
	$NOPF_6$	SO_2		> 7.34	73
	$NOSbCl_6$	SO_2		7.81	73
	$NOTiCl_4$	SO_2		7.60 (0.19)	72
Toluene	$NOAlCl_4$	SO_2	2.67 (0.37)	7.92 (0.72)	72
	see [b]	see [c]	2.52 (0.14)	7.57 (0.31)	78
	$NOPF_6$	SO_2	2.42 (0.12)	7.38, 7.45	73
	$NOSbCl_6$	SO_2	2.78 (0.48)	8.05 (0.85)	73
	$NOSbCl_6$ (see [d])	SO_2	2.47 (0.17)	7.46 (0.26)	73
	$(NO)_2SnCl_4F_2$	SO_2	2.56 (0.26)	7.65, 7.74	72
	$NOTaCl_6$	SO_2	2.57	7.70–7.82	74
p-Xylene	$NOAlCl_4$	SO_2	2.63 (0.35)	7.81 (0.70)	72
	$NONbCl_6$	SO_2	2.57	7.67	74
	$NONbF_6$	SO_2	2.45	7.43	74
	$NOPF_6$	SO_2	2.55 (0.27)	7.63 (0.52)	73
	$NOSbCl_6$	SO_2	2.58 (0.30)	7.67 (0.56)	73
	$(NO)_2SnCl_4F_2$	SO_2	2.67 (0.39)	7.83 (0.72)	72
	$NOTaCl_6$	SO_2	2.44	7.40	74
	$NOTiCl_6$	SO_2	2.38 (0.10)	7.30 (0.19)	72

Table 3 (continued).

Compound	Salt	Solvent	Chemical shifts (δ_H) [a]		Ref.
			CH_3	H_{arom}	
Mesitylene	$NOAlCl_4$	SO_2	2.58 (0.35)	7.58 (0.77)	72
	see [b]	see [c]	2.52 (0.24)	7.49 (0.66)	78
	$NONbCl_6$	SO_2	2.52	7.44	74
	$NONbF_6$	SO_2	2.41	7.18	74
	$NOPF_6$	SO_2	2.52 (0.29)	7.45 (0.64)	73
	$NOPF_6$	CD_3NO_2	2.51	7.50	76
	$(NO)_2SnCl_6$	SO_2	2.42 (0.19)	7.21 (0.40)	72
	$(NO)_2SnCl_4F_2$	SO_2	2.60 (0.37)	7.57 (0.76)	72
	$NOTaCl_6$	SO_2	2.58	7.57	74
	$NOTaF_6$	SO_2	2.51	7.40	74
Durene	see [b]	see [c]	2.48 (0.30)	7.67 (0.78)	78
	$NOPF_6$	CD_3NO_2 (see [e])	2.37 (0.19)	7.42 (0.54)	62
	$NOPF_6$	CD_3NO_2	2.43	7.56	76
tert-Butylbenzene	$NOSbl_6$	SO_2	1.47 (0.17)	7.89, 7.96, 8.05	73
Pentamethylbenzene	see [b]	see [c]	2.44 (0.28), 2.46 (0.26)	7.66 (0.87)	78
	$NOPF_6$	CD_3NO_2 (see [e])	2.38 (0.20), 2.44 (0.23)	7.52 (0.71)	62
	$NOPF_6$ (see [d])	CD_3NO_2 (see [e])	2.27 (0.09), 2.31 (0.10)	7.1 (0.29)	62
	$NOPF_6$	CD_3NO_2	2.44, 2.51	7.66	76
Hexamethylbenzene	$NOAlCl_4$	SO_2	2.48 (0.33)		72
	$NOAsF_6$	SO_2	2.39 (0.24)		73
	$NOBF_4$	SO_2	2.42 (0.27)		72
	$(NO)_2GeCl_2F_4$	SO_2	2.45 (0.30)		72
	$(NO)_2GeF_6$	SO_2	2.32 (0.17)		72
	$NOMoCl_6$	SO_2	2.21		74
	$NOMoF_6$	SO_2	2.40		74
	$NOMo_2O_2F_9$	SO_2	2.46		74
	$NONbCl_6$	SO_2	2.49		74
	$NONbF_6$	SO_2	2.46		74
	$NOPF_6$	SO_2	2.47 (0.32)		73
	$NOPF_6$	CD_3CN	2.48 (0.30)		78
	$NOPF_6$	CD_3CN	2.48		76
	$NOSbCl_6$	SO_2	2.47 (0.32)		73
	$NOSbF_6$	SO_2	2.48 (0.33)		73
	$(NO)_2SiF_6$	SO_2	2.42 (0.27)		72
	$(NO)_2SnCl_6$	SO_2	2.49 (0.34)		72
	$(NO)_2SnCl_4F_2$	SO_2	2.50 (0.35)		72
	$NOTaCl_6$	SO_2	2.48		74
	$NOTaF_6$	SO_2	2.47		74
	$(NO)_2TiCl_6$	SO_2	2.50 (0.35)		72
	$(NO)_2TiF_6$	SO_2	2.48 (0.33)		72
	$NOUF_6$	SO_2	2.34		74
	$NOUF_7$	SO_2	2.47		74
	$NOWCl_7$	SO_2	2.46		74
	$NOW_2O_2F_9$	SO_2	2.42		74
Chlorobenzene	$NOGaCl_4$	SO_2		7.38	72

[a] The differences between the chemical shifts of the signals for the protons in the spectra of the π-complex and its precursor are given in parentheses. [b] Either $NOBF_4$ or $NOPF_6$ was used as the salt. [c] Either CD_3CN or CD_3NO_2 was used as the solvent. [d] The ArH : $[NO]^+X^-$ molar ratio was 2 : 1. [e] The reaction temperature was 35 °C; in all other cases, the temperature was not reported.

Table 4. ^{13}C NMR spectral data for the π-complexes of benzene and its derivatives with the nitrosonium cation (the molar ratio ArH : $[NO]^+X^-$ = 1 : 1).

Compound	Salt	Solvent	Chemical shifts (δ_C) [a]		Ref.
			CH_3	C_{arom}	
Benzene	$NOAlCl_4$	SO_2		137.1 (7.9)	72
	see [b]	see [c]		131.0 (1.2)	78
	$NOGaCl_4$	SO_2		134.8 (5.6)	72
	$NOPF_6$	SO_2		> 129.1	73
	$NOTiCl_4$	SO_2		132.2 (3.0)	72
	$NOSbCl_6$	SO_2		136.7 (7.5)	73

Table 4 (continued).

Compound	Salt	Solvent	Chemical shifts (δ_C) [a]		Ref.
			CH_3	C_{arom}	
Toluene	see [b]	see [c]	21.7 (0)	132.5 (4.8), 135.1 (5.1), 136.1 (5.7), 147.6 (8.0)	78
	$NOPF_6$	SO_2	20.9 (0.1)	128.4, 131.3, 132.1, 142.0	73
	$NOSbCl_6$ (see [d])	SO_2	20.8	129.8, 132.6, 133.2, 144.3	73
	$(NO)_2SnCl_4F_2$	SO_2	21.3 (0.5)	132.6, 135.1, 136.0	72
	$NOTaCl_6$	SO_2	21.4	133.7, 136.1, 137.0, 149.3	74
p-Xylene	$NOPF_6$	SO_2	20.7	137.6, 147.6	73
	$NONbF_6$	SO_2	20.6	135.0 [e]	74
	$NOSbCl_6$	SO_2	20.8	137.8, 148.0	73
	$(NO)_2SnCl_4F_2$	SO_2	21.1	139.9, 151.1	72
	$NOTaF_6$	SO_2	20.6	134.3, 142.5	74
Mesitylene	$NOAlCl_4$	SO_2	see [f]	139.1 [e]	72
	see [b]	see [c]	21.6 (0.1)	137.8 (9.6), 151.8 (12.5)	78
	$NOPF_6$	SO_2	20.9	137.1, 151.1	73
	$NONbF_6$	SO_2	20.7	132.9, 145.5	74
	$NOTaCl_6$	SO_2	21.2	138.9, 153.4	74
	$NOTaF_6$	SO_2	20.9	136.1, 149.8	74
	$(NO)_2TiCl_6$	SO_2	20.9	135.2 (4.7) [e]	72
Durene	$NOAlCl_4$	CH_2Cl_2 (see [g])	19.8	142.0, 150.3	71
	see [b]	see [c]	19.7 (0.4)	142.9 (10.6), 151.3 (16.2),	78
	$NOAlCl_4$	see [g, h]	20.1	148.3, 154.5	71
tert-Butylbenzene	$NOSbCl_6$	SO_2	30.5, 36.5	134.3, 134.8, 136.9, 163.5	73
Pentamethylbenzene	see [b]	see [c]	21.1 (0.3), 17.3 (0.9), 16.9 (0.8)	141.5 (11.3), 151.0 (17.4), 151.5 (17.0), 152.8 (16.7)	78
Hexamethylbenzene	$NOAlCl_4$	CH_2Cl_2 (see [g])	17.5	147.7	71
	$NOAlCl_4$	SO_2	17.3 (1.6)	149.9 (18.9)	72
	$NOAlCl_4$	see [g, h]	18.6	142.1	71
	$NOAsF_6$	SO_2	17.1 (1.4)	149.1 (18.1)	73
	$(NO)_2GeF_6$	SO_2	16.7 (1.0)	142.1 (11.1)	72
	$NOMoCl_6$	SO_2	16.5	131.7	74
	$NOMoF_6$	SO_2	17.1 (1.4)	147.9 (16.9)	74
	$NOMo_2O_2F_9$	SO_2	17.1 (1.4)	148.6 (17.6)	74
	$NONbF_6$	SO_2	17.1 (1.4)	148.1 (17.1)	74
	$NOPF_6$	SO_2	17.1 (1.4)	149.8 (18.8)	73
	$NOPF_6$	CD_3NO_2	17.9 (0.9)	150.8 (17.6)	78
	$NOSbCl_6$	SO_2	18.2 (2.5)	150.2 (19.2)	73
	$NOSbCl_6$	see [h]	20.5	151.9	78
	$NOSbF_6$	SO_2	17.1 (1.4)	150.1 (19.1)	73
	$(NO)_2SiF_6$	SO_2	16.9 (1.2)	144.6 (13.6)	72
	$(NO)_2SnCl_4F_2$	SO_2	17.3 (1.6)	150.2 (19.2)	72
	$NOTaCl_6$	SO_2	17.5 (1.8)	150.3 (19.3)	74
	$NOTaF_6$	SO_2	17.2 (1.5)	149.8 (18.8)	74
	$(NO)_2TiCl_6$	SO_2	17.3 (1.6)	150.2 (19.2)	72
	$(NO)_2TiF_6$	SO_2	17.1 (1.4)	148.8 (17.8)	72
	$NOUF_6$	SO_2	17.2 (1.5)	143.7 (12.7)	74
	$NOUF_7$	SO_2	17.3 (1.6)	149.5 (18.5)	74
	$NOWCl_7$	SO_2	17.7 (2.0)	150.5 (19.5)	74
	$NOW_2O_2F_9$	SO_2	17.4 (1.7)	146.9 (15.9)	74

[a] The differences between the chemical shifts of the signals for the carbon atoms in the spectra of the π-complex and its precursor are given in parentheses. [b] Either $NOBF_4$ or $NOPF_6$ was used as the salt. [c] Either CD_3CN or CD_3NO_2 was used as the solvent. [d] The $ArH : [NO]^+X^-$ molar ratio was 2 : 1. [e] The chemical shift is given only for the CH fragment. [f] The chemical shift was not reported. [g] The reaction temperature was 20 °C; in all other cases, the temperature was not reported. [h] For the crystalline form.

Table 5. Data from IR (ν_{NO}) and electronic absorption spectroscopy (λ_{max}) of the π-complexes of benzene and its derivatives with the nitrosonium cation (the molar ratio $ArH : [NO]^+X^- = 1 : 1$).

Compound	Reagent	Solvent	ν_{NO} /cm^{-1}	λ_{max} /nm (ε)	Ref.
Benzene	$NOAlCl_4$	CH_2Cl_2	–	335	72
	$NOHSO_4$	H_2SO_4	–	332 (18 000)	64
	$NOBF_4$	MeCN	–	346 (780), 460 (60)	76, 78
	$NOGaCl_4$	CH_2Cl_2	–	335	72

Table 5 (continued).

Compound	Reagent	Solvent	ν_{NO} /cm^{-1}	λ_{max} /nm (ε)	Ref.
Benzene	$NOPF_6$	$MeNO_2$	2075	–	78
	$NOSbCl_6$	–	–	344	73
Toluene	$NOAlCl_4$	CH_2Cl_2	–	338 (11 000)	72
	$NOBF_4$	MeCN	–	342 (400)	76, 78
	$NOPF_6$	$MeNO_2$	2037	–	78
	$NOSbCl_6$	$MeNO_2$	2030	–	78
Toluene	$NOSbCl_6$	–	–	340 (10 600)	73
	$NOSbCl_6$	–	–	340 (5300) [a]	73
o-Xylene	$NOBF_4$	MeCN	–	338 (2200), 500 (180)	78
	$NOPF_6$	$MeNO_2$	2000	–	78
p-Xylene	$NOAlCl_4$	CH_2Cl_2	–	340	72
	$NOBF_4$	MeCN	–	336 (1300), 520 (81)	78
	$NOBF_4$	CH_2Cl_2	–	496 [b]	83
	N_2O_4	CH_2Cl_2	1964 [c]	–	83
	$N_2O_4(SbCl_6)$	CH_2Cl_2	–	506 [b]	83
	$NOPF_6$	$MeNO_2$	1998	–	78
	$NONbF_6$	see [d]	1810	–	74
	$NOTaF_6$	see [d]	1810	–	74
	$NOTaF_6$	CH_2Cl_2	–	274, 446	74
	$NOSbCl_6$	CH_2Cl_2	–	340 (10 000)	73
Mesitylene	$NOAlCl_4$	CH_2Cl_2	–	343	72
	$NOBF_4$	MeCN	–	345 (2080)	76
	$NOBF_4$	MeCN	–	345 (2100)	78
	$NOBF_4$	$MeNO_2$	2000 – 1950	–	62
	$NOBF_4$	CH_2Cl_2	–	486 [b]	83
	N_2O_4	CH_2Cl_2	1948 [c]	–	83
	$N_2O_4(SbCl_6)$	see [e]	1954	–	83
	$N_2O_4(SbCl_6)$	CH_2Cl_2	–	493 [b]	83
	$NONbF_6$	CH_2Cl_2	–	386	74
	$NOPF_6$	CH_2Cl_2	1967	335	76
	$NOPF_6$	$MeNO_2$	1975	–	78
	$NOPF_6$	see [f]	2016	–	76
	$NOSbCl_6$	$MeNO_2$	1964	–	78
	$(NO)_2SiF_6$	CH_2Cl_2	–	390	72
	$(NO)_2SnCl_4F_2$	CH_2Cl_2	–	391	72
	$NOTaF_6$	CH_2Cl_2	–	388	74
	$(NO)_2TiCl_6$	CH_2Cl_2	–	285	72
tert-Butylbenzene	$NOBF_4$	MeCN	–	340 (270), 460 (52)	78
	$NOSbCl_6$	–	–	339 (5000)	73
	$(NO)_2SnCl_6$	CH_2Cl_2	–	360	72
1,3,5-Tri-*tert*-butylbenzene	$NOBF_4$	MeCN	–	349 (1730)	76
	$NOBF_4$	MeCN	–	349 (1700)	78
	$NOPF_6$	$MeNO_2$	1964	–	78
Durene	$NOBF_4$	MeCN	–	336 (1100), 520 (40)	78
	$NOBF_4$	CH_2Cl_2	–	486 [b]	83
	N_2O_4	CH_2Cl_2	1948 [c]	–	83
	$N_2O_4(SbCl_6)$	see [e]	1880	–	83
	$N_2O_4(SbCl_6)$	CH_2Cl_2	–	489 [b]	83
	$NOPF_6$	$MeNO_2$	1933	–	62, 78
	$NOPF_6$	CH_2Cl_2	1929	335, ~500	76
	$NOPF_6$	MeCN	1930	–	62
	$NOPF_6$	$MeNO_2$	1930	–	62
	$NOPF_6$	MeCN or $MeNO_2$	–	335	62
	$NOPF_6$	see [f]	1986	–	76
Pentamethylbenzene	$NOBF_4$	MeCN	–	337 (2400)	76, 78
	$NOBF_4$	CH_2Cl_2	–	491 [b]	83
	N_2O_4	CH_2Cl_2	1896 [c]	–	83
	$N_2O_4(SbCl_6)$	CH_2Cl_2	–	490 [b]	83
	$NOPF_6$	MeCN or $MeNO_2$	–	340	62
	$NOPF_6$	CH_2Cl_2	1904	–	76
	$NOPF_6$	MeCN	1900	–	62
	$NOPF_6$	$MeNO_2$	1900	–	62
	$NOPF_6$	$MeNO_2$	1907	–	78
	$NOPF_6$	see [f]	1927	–	76

Table 5 (continued).

Compound	Reagent	Solvent	ν_{NO} /cm^{-1}	λ_{max} /nm (ε)	Ref.
Hexamethylbenzene	$NOAlCl_4$	see [d]	1853	–	71
	$NOAlCl_4$	CH_2Cl_2	–	334 (10 000)	72
	$NOAsF_6$	–	–	334 (47 000)	73
	$NOBF_4$	MeCN	–	337 (3000)	76
	$NOBF_4$	MeCN	–	337 (3100)	78
	$NOBF_4$	CH_2Cl_2	–	325 (7300), 499 [b]	72, 83
	$(NO)_2GeF_6$	CH_2Cl_2	–	338 (7100)	72
	$NOFeCl_4$	CH_2Cl_2	–	325, 360	74
	$NOMo_2O_2F_9$	CH_2Cl_2	–	323	74
	$NOMo_2O_2F_9$	see [d]	1870	–	74
	$NOMoF_6$	see [d]	1780	–	74
	N_2O_4	CH_2Cl_2	1862 [c]	495 [b]	83
	$N_2O_4(SbCl_6)$	see [e]	1850	–	83
	$N_2O_4(SbCl_6)$	CH_2Cl_2	–	499 [b]	83
	$NOPF_6$	CH_2Cl_2	1880	337, ~500	76
	$NOPF_6$	–	–	275 [g]	73
	$NOPF_6$	$MeNO_2$	1885	–	78
	$NOPF_6$	see [f]	1899	–	76
	$NONbF_6$	see [d]	1850	–	74
	$NONbF_6$	CH_2Cl_2	–	330	74
	$NOSbCl_6$	see [d]	1849	–	73
	$NOSbCl_6$	–	–	334 (8100)	73
	$NOSbCl_6$	$MeNO_2$	1885	–	78
	$NOSbF_6$	see [d]	1850	–	73
	$NOSbF_6$	CH_2Cl_2	–	330	55
	$NOSbF_6$	–	–	272	73
	$(NO)_2SiF_6$	CH_2Cl_2	–	338	72
	$(NO)_2SnCl_6$	CH_2Cl_2	–	336	72
	$(NO)_2SnCl_4F_2$	CH_2Cl_2	–	336	72
	$NOTaCl_6$	CH_2Cl_2	–	332	74
	$NOTaF_6$	see [d]	1800	–	74
	$NOTaF_6$	CH_2Cl_2	–	334	74
	$NOTiCl_6$	CH_2Cl_2	–	310	72
	$(NO)_2TiCl_4F_2$	CH_2Cl_2	–	340	72
	$(NO)_2TiF_6$	CH_2Cl_2	–	326	72
	$NOUF_6$	see [d]	1880	–	74
	$NOUF_6$	CH_2Cl_2	–	320	74
	$NOUF_7$	see [d]	1870	–	74
	$NOUF_7$	CH_2Cl_2	–	325	74
	$NOWCl_7$	CH_2Cl_2	–	358	74
	$NOW_2O_2F_9$	see [d]	1878	–	74
Hexaethylbenzene	$NOBF_4$	CH_2Cl_2	–	511 [b]	83
	$NOPF_6$	$MeNO_2$	1900	–	78
	N_2O_4	CH_2Cl_2	–	516 [b]	83
1,3-Dineopentyl-2,4,5,6-tetramethylbenzene	$NOPF_6$	$MeNO_2$	1884	–	78
1,4-Dineopentyl-2,3,5,6-tetramethylbenzene	$NOPF_6$	$MeNO_2$	1884	–	78
Anisole	$NOBF_4$	MeCN	–	344 (1000), 480 (635) [h]	84
Chlorobenzene	$NOBF_4$	MeCN	–	343 (110), 500 (6.4)	78
	$NOGaCl_4$	CH_2Cl_2	–	290 [g]	72
2-Methylanisole	$NOBF_4$	MeCN	–	346, 477 [h]	84
4-Methylanisole	$NOBF_4$	MeCN	–	346 (980), 506 (370) [h]	84
	$NOBF_4$	CH_2Cl_2	–	334	78
3,5-Dimethylanisole	$NOBF_4$	MeCN	–	355, 488 [h]	84
2-Bromoanisole	$NOBF_4$	MeCN	–	353, 463 [h]	84
4-Bromoanisole	$NOBF_4$	MeCN	–	340 (470), 500 (100) [h]	84
1,4-Dimethoxybenzene	$NOBF_4$	CH_2Cl_2	–	366 [c]	85

[a] The ArH : $[NO]^+X^-$ molar ratio was 2 : 1. [b] The λ_{max} value is given only for the long-wavelength band (at −78 °C). [c] At −78 °C. [d] In KBr pellets. [e] Mineral oil mull. [f] Spectra of the crystalline form. [g] Shoulder. [h] At −40 °C.

The degree of electron density transfer can be estimated from ^{13}C NMR spectral data. It is known that the chemical shifts of the sp^2-hybridised carbon atoms in charged π-electron systems correlate linearly with the π-charges on these atoms.[102, 103] Assuming that the degree of electron density transfer to the nitroso group in the π-complex depends on the ionisation potential of the aromatic substrate (I_p), one would expect a relationship between the positive π-charges (q_π^+) and the ionisation potentials of the aromatic donor.[78] Actually, a linear correlation between these characteristics takes place in the case of the nitrosonium π-complexes of benzene and alkylbenzenes [78] (Fig. 2) from which it can be seen that an increase in the donating ability of the aromatic substrate leads to an increase in the degree of charge transfer.

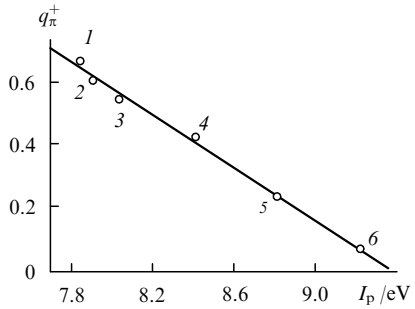


Figure 2. Correlation between the positive π-charges (q_π^+) on the aromatic fragments in the nitrosonium complexes with benzene and alkylbenzenes and the ionisation potentials (I_p) of the aromatic donors:[78] (*1*) hexamethylbenzene, (*2*) pentamethylbenzene, (*3*) durene, (*4*) mesitylene, (*5*) toluene, (*6*) benzene ($r = -0.998$). The q_π^+ values were calculated using the differences between the chemical shifts of the complexes and their precursors determined in the study;[78] the value of 160 ppm was taken per unit π-charge.

It was demonstrated[78] that the degree of charge transfer in π-complexes can be estimated by IR spectroscopy. Thus a linear correlation between the ionisation potentials of the aromatic substrate and the degree of charge transfer (Z) was found for benzene and its derivatives. The degree of charge transfer was determined from the following formula:

$$Z = (\nu_{NO^+}^2 - \nu_\pi^2)/(\nu_{NO^+}^2 - \nu_{NO}^2),$$

where ν_{NO^+}, ν_π and ν_{NO} are stretching vibration frequencies of the NO group in the NO^+ cation, the π-complex and nitric oxide, respectively (Fig. 3).[78]

X-Ray diffraction studies provide the most reliable information on the structures of cationic complexes. The first data on the structures of nitrosonium complexes of aromatic compounds obtained[68,69] for the complex of hexamethylbenzene with the NO^+ cation disclosed that the conventional view (*cf.* Refs 61 and 64) that π-complexes of aromatic compounds with electrophilic agents are highly symmetrical systems should be revised.[104] According to the X-ray diffraction data,[68,71] the normal (which passes through the nitrogen atom of the NO group) to the plane of the core of this complex is displaced from the centre of the aromatic ring and the nitroso group is located at an angle of ~50° (the structure **38**), the nitrogen atom being rather far removed from the ring (by 0.21 nm).

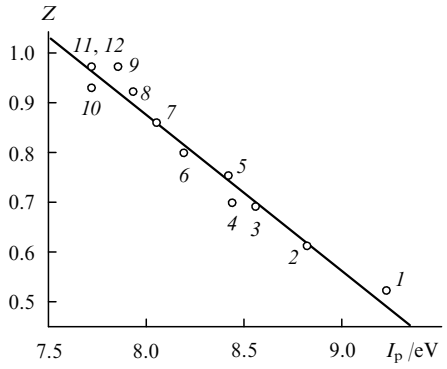
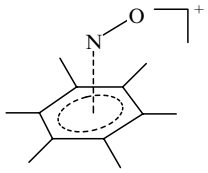


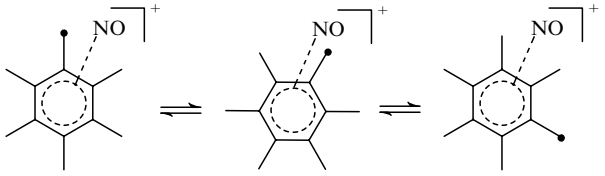
Figure 3. Correlation between the degree of electron transfer (Z) in nitrosonium complexes with benzene and alkylbenzenes and the ionisation potentials (I_p) of the aromatic donors: (*1*) benzene, (*2*) toluene, (*3*) 1,2-dimethylbenzene, (*4*) 1,4-dimethylbenzene, (*5*) 1,3,5-trimethylbenzene, (*6*) 1,3,5-tri(*tert*-butyl)benzene, (*7*) 1,2,4,5-tetramethylbenzene, (*8*) pentamethylbenzene, (*9*) hexamethylbenzene, (*10*) hexaethylbenzene, (*11*) 1,4-di(neopentyl)-2,4,5,6-tetramethylbenzene, (*12*) 1,3-di(neopentyl)-2,3,5,6-tetramethylbenzene ($r = -0.987$).[78]



38

The nitrosonium complexes of toluene,[73] mesitylene,[78] durene,[71] hexaethylbenzene,[88] 2,3-dimethyl-2,3-diphenylbutane,[81] 1,2,3,4,5,6,7,8,9,10,11,12-dodecahydro-1,4;5,8;9,12-triethanotriphenylene[88] and octamethyl-9,10-dihydro-9,10-ethanoanthracene[105] have analogous structures. A comparison of the structures and geometric parameters of nitrosonium complexes of arenes and alkenes disclosed that these complexes are somewhat similar, *viz.*, the NO group is located at an angle to the plane of the core and the distances from the nitrogen atom to this plane have close values.

According to the results of CNDO/2 calculations with the use of the real geometry of the hexamethylbenzene complex with the nitrosonium cation, the positive charges on the aromatic carbon atoms of the same type differ substantially from those on the carbon atoms of the methyl groups.[71] Nevertheless, two rather narrow singlets are observed in the ^{13}C NMR spectra recorded both for solutions (in the HSO_3F-SO_2ClF mixture, −130 °C)[75] and for the solid phase,[71] which is attributable to the π,π-rearrangement, rapid within the NMR time scale.



38 **38′** **38″**

The mechanism of this rearrangement involves either the migration of the NO group over the plane of the ring or the rotation of this ring about its 'normal' followed by 'switching' of the $C_{arom}-N$ bonds, the latter situation being more probable for the complex in the crystalline state.[71,75] The results of studies of the isotope effects of deuterium manifested in the ^{13}C NMR spectra of nitrosonium π-complexes with $C_6(CD_3)_m(CH_3)_{6-m}$ compounds do not contradict the conclusion that these complexes undergo rapid π,π-rearrangement in solutions.[80] The kinetic parameters of this rearrangement ($E_a = 42.7\pm2.5$ kJ mol^{-1}, $\log A = 13.9\pm0.3$) for the crystalline complex were determined by relaxation NMR spectroscopy.[75]

According to the ^1H and ^{13}C NMR spectral data, analogous π,π-rearrangements occur, apparently, in the nitrosonium complexes of benzene,[72,73,78] alkylbenzenes,[62,72–74,76,78] chlorobenzene,[72] anisole,[87] 2,3,5,6,8,9-hexahydro-1,2;3,4;5,6-tris(cyclopenta)benzene,[106] [2.2]paracyclophane[107] and triptycene.[107]

To reveal the contributions of the intermolecular and intramolecular mechanisms of rearrangements of nitrosonium complexes, it is important to elucidate the influence of the structure of the aromatic substrate on the formation constants of these complexes (K):

$$ArH + NO^+ \overset{K}{\rightleftharpoons} ArH-NO^+.$$

The quantitative data on the constants K for the π-complexes of benzene and its derivatives were obtained[76,78,81,84,88] by processing electronic absorption spectra using the Benesi–Hildebrand method. A linear correlation between the logarithms of the formation constants of the π-complexes and the ionisation potentials of the corresponding aromatic hydrocarbons was found[76] (Fig. 4). The point corresponding to 1,3,5-tri(*tert*-butyl)benzene deviates from the dependence presented in Fig. 4[76] due, appa-

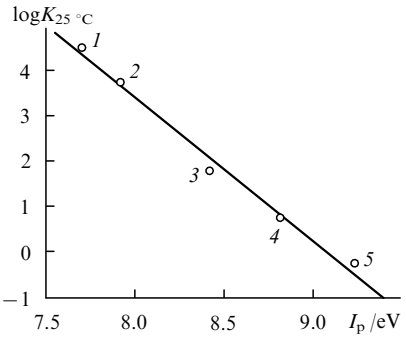


Figure 4. Dependence of the logarithms of the formation constants ($\log K$) of the $ArH-NO^+$ complexes (BF_4^- as the anion) in MeCN at 25 °C on the ionisation potentials (I_p) of the aromatic donors: (*1*) hexamethylbenzene (*2*) pentamethylbenzene (*3*) mesitylene (*4*) toluene (*5*) benzene ($r = -0.995$).[76]

rently, to steric inhibition of the donor-acceptor interaction between the aromatic substrate and the nitrosonium cation (*cf.* Ref. 88).

The high degree of charge transfer in the ground state of nitrosonium complexes of aromatic compounds containing donor substituents agrees well with the chemical behaviour of these complexes. The key stage of these reactions involves the transfer of one electron from the aromatic donor to the NO^+ group giving rise to a radical cation, which undergoes further transformations:

$$ArH + NO^+ \rightleftharpoons [ArH, NO^+],$$

$$[ArH, NO^+] \rightleftharpoons [ArH^{+\bullet}, NO^\bullet],$$

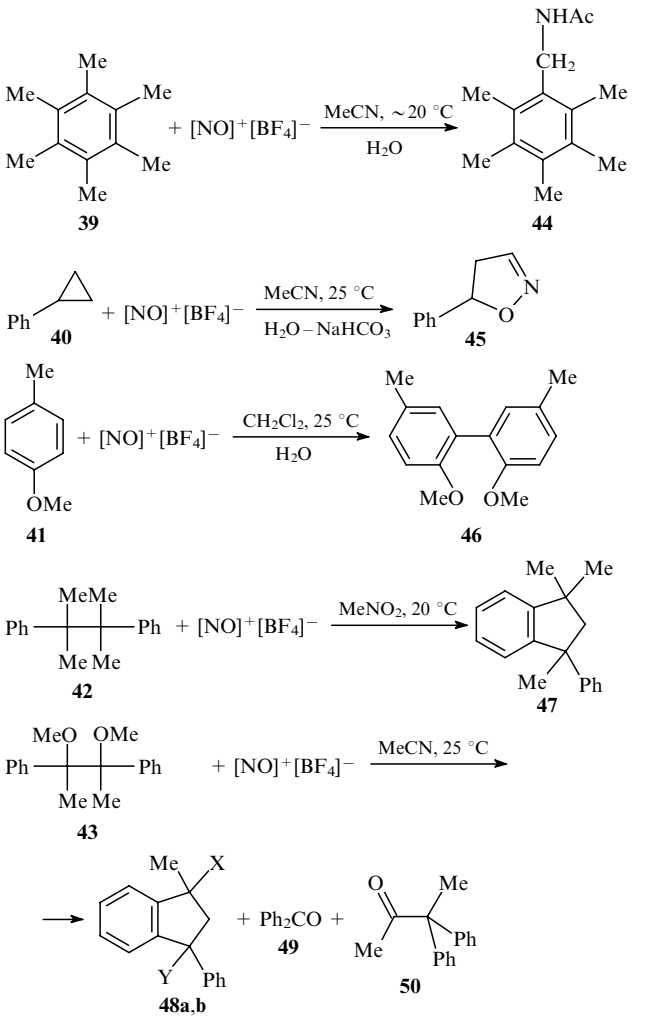
$$[ArH^{+\bullet}, NO^\bullet] \longrightarrow \text{products}.$$

This general scheme can be exemplified by the conversions of aromatic compounds **39**–**43** into products **44**–**50** (Scheme 4). In these processes, $ArH-NO^+$ π-complexes are, apparently, generated at the initial stage (see Refs 78 and 81).

All the above-considered calculated and experimental data provide evidence that the reactions of the nitrosonium cation with monocyclic aromatic compounds generally afford π-complexes rather than σ-complexes. In this connection, it is of interest that investigation of the kinetics of nitrosodeiodination of 4-iodoanisole by electronic absorption spectroscopy [63] provided evidence for the formation of the σ-complex, *viz.*, the 1-iodo-4-methoxy-1-nitrosobenzenonium ion (*cf.* Ref. 91). Recently, the nitrosonium σ-complexes with benzene, mesitylene, hexamethylbenzene and other aromatic compounds have been detected by this method using the femtosecond laser technique at low temperature.[90] However, it is known that information on the structures of cationic complexes of aromatic compounds obtained by electronic absorption spectroscopy is less reliable than that provided by NMR spectroscopy.[103] The more reliable NMR spectral data demonstrated that the reactions of anisole [87] and hexamethylbenzene [80] with $[NO]^+[AlCl_4]^-$ in the $SO_2-CD_2Cl_2$ system at low temperature afforded π-complexes (*cf.* Refs 68 and 71–76).

The nitrosonium cation is a strong oxidising agent [108, 109] (*cf.* Refs 55 and 56). Generally, its reactions with bi- and polycyclic arenes possessing, as a rule, low ionisation potentials [110] give rise to the corresponding radical cations or their reaction products.[55, 78, 109] Thus, the reactions of naphthalene with nitrosonium salts in trifluoroacetic acid at ~20 °C afforded initially a monomeric radical cation, followed by the formation of a dimeric radical cation and, finally, of a mixture of hydrocarbons $C_{10}H_7-(C_{10}H_6)_m-C_{10}H_7$.[109, 111, 112] Most likely, the transfer of one electron from the aromatic substrate to the NO^+ cation is preceded by the formation of the $ArH-NO^+$ π-complex. In spite of the importance of the data on the structures and reactivities of nitrosonium complexes with polycyclic aromatic compounds,

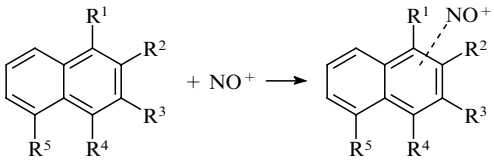
Scheme 4



48a: X = OMe, Y = Me;
48b: X = Y = OMe.

attempts to generate these complexes have long been unsuccessful.[61, 76, 113–117]

The first data on the formation of nitrosonium π-complexes with fused arenes were obtained for derivatives of naphthalene,[113, 114] fluorene [113] and acenaphthylene [114] (*cf.* Refs 55 and 76). The reactions of $[NO]^+[AlCl_4]^-$ with methylnaphthalenes **51a**–**i** in SO_2 at low temperatures (from −70 to −80 °C) afforded cationic π-complexes **52a**–**i**, respectively.[115, 116]



51a–**i** **52a**–**i**

Compounds **51**, **52**	R^1	R^2	R^3	R^4	R^5
a	H	H	H	H	H
b	Me	H	H	H	H
c	H	Me	H	H	H
d	Me	Me	H	H	H
e	Me	H	Me	H	H
f	Me	H	H	Me	H
g	Me	H	H	H	Me
h	H	H	H	Me	Me
i	H	Me	Me	H	H

Table 6. Parameters of the ^{13}C NMR spectra (δ_C) of the complexes **57a**,**c**–**f** [117, 119] and the charges q_π^+ on the C(3)–C(8b) atoms.

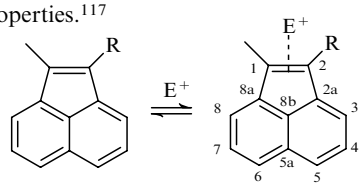
Complex	System or solvent	Temperature /°C	$\delta_{C(1)}$, $\delta_{C(2)}$ (see [a])	$\Delta\sum\delta_{C(3)-C(8b)}$ (see [b])	q_π^+ (see [c])
57a	HSO_3F-SO_2	−70	170.8	33.9	0.21
		−40	171.3	35.4	0.22
57c	SO_2-SO_2ClF	−95	153.6, 168.0	–	–
57d	SO_2	−80	150.6, 166.4	41.6	0.26
57e	CD_2Cl_2	−80	80.8	10.1	0.06
57f	HSO_3F-SO_2ClF	−50	98.3	17.4	0.11

[a] The chemical shifts are given relative to Me_4Si; CD_2Cl_2 was used as the internal standard (δ 52.9). [b] The difference between the total chemical shifts of the signals for the C(3)–C(8b) atoms in the spectra of the π-complex and its precursor. [c] In calculations, the value of 160 ppm was taken per unit π-charge.[102]

The structures of these complexes were confirmed by the results of ^1H, ^{13}C and ^{15}N NMR spectroscopy using the isotope perturbation method.[116] The equivalence of the methyl groups in the π-complexes **52f**–**i** observed in the ^1H NMR spectra was attributed [116] to the rapid (within the NMR time scale) intra- and(or) intermolecular migration of the NO group from one aromatic ring to another.

Apparently, analogous rearrangements occur in the nitrosonium complexes of fluorene (**53**),[113] [2.2]paracyclophane (**54**),[107] triptycene (**55**) [107] and corannulene (**56**) [118] (Scheme 5).

Unlike the complexes of the nitrosonium ion **52**–**56**, the nitrosonium complexes with 1-R-2-methylacenaphthylene (R = Me, CH_2D, CH_2Cl or Br) **57a**–**d** do not exhibit dynamical properties.[117]



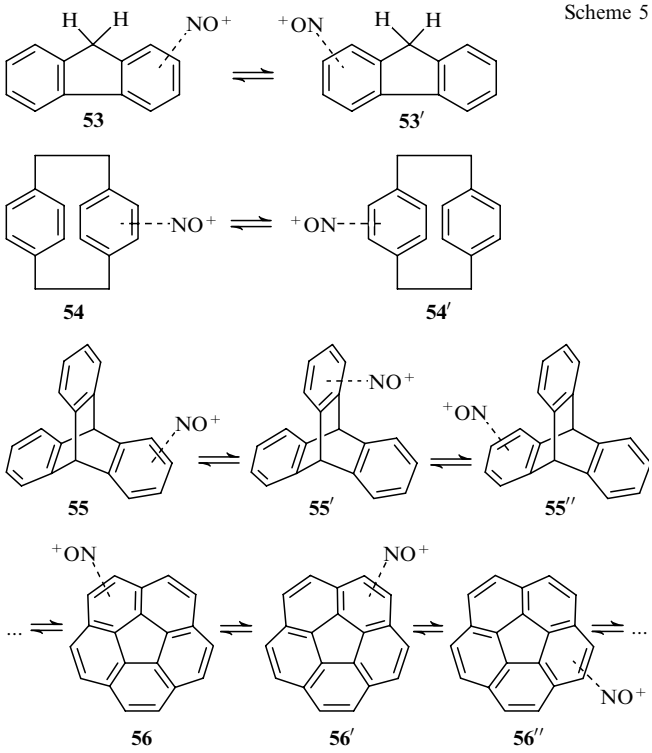
57a–**f**

Compound **57**	E	R
a	NO	Me
b	NO	CH_2D
c	NO	CH_2Cl
d	NO	Br
e	MeS	Me
f	PhS	Me

This is evidenced by the ^1H, ^{13}C and ^{15}N NMR spectral data and by the results obtained by the isotope perturbation method.[117] The fact that the signals for the C(1) and C(2) atoms in the π-complexes **57a**–**d** are shifted downfield compared to those of their analogues, *viz*., the episulfonium ions **57e**,**f** [119] (Table 6), was taken [117] as convinicng evidence for the preferential localisation of the NO group at the C(1)–C(2) bond assuming that the C(1) and C(2) atoms have nearly sp^2-hybridisation.

Substantial electron density transfer from the aromatic fragment to the NO^+ group is observed in the complexes of acenaphthylene and naphthalene derivatives (Table 7, see Table 6), as in nitrosonium complexes of monocyclic aromatic compounds containing donor substituents.[78] The greater the number of methyl groups in the rings of the complexes **52a**–**i**, the higher the degree of transfer.[116, 117] In addition, judging from the difference between the total chemical shifts of the signals for the C(1)–C(4) and C(5)–C(8) atoms in the ^{13}C NMR spectra of the π-complex and its precursor, the positive charge is localised predominantly at the methylated aromatic ring. Interestingly, an approximate linear correlation between the total positive π-charges on the core (q_π^+) and the oxidation potentials of the precursors ($E_{1/2}$) is observed for the nitrosonium complexes of naphthalene and its derivatives (Fig. 5, see Table 7). As expected, a decrease in the oxidation potential of the aromatic hydrocarbon leads to an increase in the positive π-charge on the aromatic fragment of the π-complex **52**.

Scheme 5



As mentioned above, naphthalene is oxidised by the nitrosonium cation at room temperature to form the corresponding

Table 7. Parameters of the ^{13}C NMR spectra of the complexes **52a**–**i** (SO_2, −70 °C) [116] and the oxidation potentials of their precursors **51a**–**c**, **e**–**i**.

Compounds **51** and **52**	$\Delta\sum\delta_{C(1)-C(4)}/\Delta\sum\delta_{C(5)-C(8)}$ [a]	q_π^+[C(1)–C(8a)] [b]	$E_{1/2}$ /V [c]
a	25.2 / 25.2	0.34	1.54
b	44.9 / 16.2	0.40	1.43
c	40.6 / 18.6	0.39	1.45
d	60.9 / 19.7	0.54	–
e	56.2 / 16.9	0.47	1.38
f	60.8 / 15.6	0.49	1.32
g	36.2 / 36.2 [d]	0.49	1.43
h	32.7 / 32.7 [e]	0.42	1.30
i	47.2 / 16.8	0.42	1.44

[a] The ratio of the differences between the total chemical shifts of the signals for the C(1)–C(4) and C(5)–C(8) atoms in the spectra of the complexes **52a**–**i** and their precursors. [b] In calculations, the value of 160 ppm was taken per unit π-charge.[102] [c] The data were reported in Ref. 120. [d] At −75 °C. [e] At −80 °C.

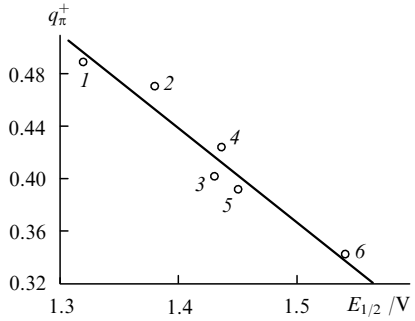
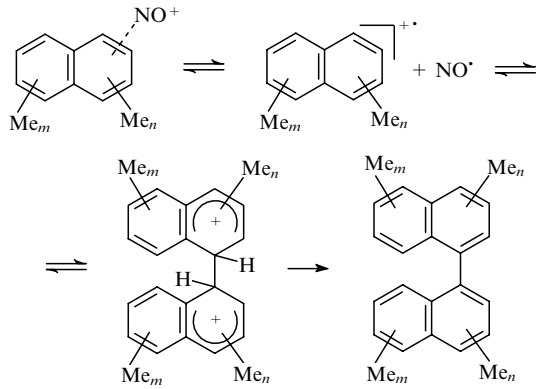


Figure 5. Correlation between the q_π^+ values for the π-complexes **52a**–**c**,**e**,**f**,**i** and the oxidation potentials ($E_{1/2}$) of their precursors **51a**–**c**,**e**,**f**,**i**:[120] (*1*) 1,4-dimethylnaphthalene, (*2*) 1,3-dimethylnaphthalene, (*3*) 1-methylnaphthalene, (*4*) 2,3-dimethylnaphthalene, (*5*) 2-methylnaphthalene, (*6*) naphthalene ($r = -0.970$). The data for the π-complexes **52g**,**h** were not taken into consideration because the q_π^+ values for the latter complexes were determined from ^{13}C NMR spectra measured at different temperatures.

radical cation.[109, 111, 112] In the case of methylnaphthalenes, an analogous process takes place at low temperature. As the temperature increases from −60 or −70 °C to −30 or −50 °C, the signals in the ^1H NMR spectra of the complexes **52a**–**i** become broader (up to their 'disappearance'), which was explained [116] by the one-electron transfer between the aromatic core of the complex and the NO group.

Dimerisation of the resulting radical cations is one of the possible conversions of these compounds.[116] Actually, storage of solutions of the complexes **52b**,**d**,**e**,**h** at −20 to −30 °C for 1–2 h followed by their treatment with water afforded 4,4′-dimethylbinaphthyl, 3,3′,4,4′-tetramethylbinaphthyl, 2,2′,4,4′-tetramethylbinaphthyl and 4,4′,5,5′-tetramethylbinaphthyl, respectively, in ~20% yields. Analogous reactions proceeded with the participation of 2-methyl-, 1-ethyl-, 2-ethyl-, 1,6-dimethyl-, 2,3-dimethyl-, 2,6-dimethyl-, 2,7-dimethyl-, 1-methoxy-, 2-methoxy-, 1-bromo- and 2-hydroxynaphthalenes (the yields of the dimeric products were 25%–95%).[121, 122]



$m = 0, 1; n = 0–2$.

V. Complexes of the nitrosonium ion with nitrogen-containing organic compounds

In a number of studies it has been suggested that nitrosonium complexes of amines and N-heterocyclic compounds are intermediates in diazotisation,[1] nitrosation of amides [1] and N-heterocyclic compounds,[123, 124] the formation [1, 125] and denitrosation [126] of nitrosoamines and other reactions involving the nitrosonium cation.[1, 127–130]

According to the results of quantum-chemical calculations [131–133] and experimental data for the gas phase,[66, 134] N-bases possess high affinities for the NO^+ cation. Thus according to the results of *ab initio* calculations [HF/6-31 + G(d)], the energy of binding of the NO^+ cation with the methylamine molecule is 127.7 kJ mol^{-1} (*cf.* Ref. 133). The data on the binding energies (E_b) of the NO^+ cation with nitriles, pyridine and the derivatives of the latter [134] were obtained by ion-cyclotron resonance and in studies of the fragmentation of $L^1(NO^+)L^2$ dimers by kinetic methods (Table 8). A linear correlation between the E_b values for alkylnitriles RCN and Taft's σ*-constants of the substituents [135] was revealed (Fig. 6). Consequently, the inductive effect of the substituents R is the major factor responsible for the stability of the $RCN-NO^+$ complexes (*cf.* Ref. 66).

Table 8. Energies of binding (E_b) of the NO^+ cation with N-bases.[134]

Compound	E_b /kJ mol^{-1}	Compound	E_b /kJ mol^{-1}
$CH_2(CN)_2$	82.0	PhCN	121.3
MeCN	110.5	*o*-MeC_6H_4CN	123.4
EtCN	115.5	3-FC_5H_4N	156.1
Pr^nCN	117.2	4-ClC_5H_4N	162.3
Pr^iCN	118.8	C_5H_5N	167.8
Bu^tCN	121.3	3-MeC_5H_4N	172.0

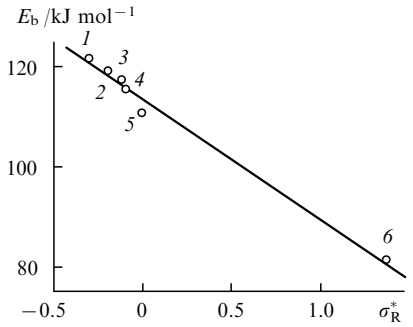


Figure 6. Correlation between the energies of binding (E_b) of the NO^+ cation with nitriles RCN [134] and the σ*-constants of the substituents R (σ_R^*),[135] where R = Bu^t (*1*), Pr^i (*2*), Pr^n (*3*), Et (*4*) or Me (*5*) and RCN = $CH_2(CN)_2$ (*6*) ($r = -0.995$).

A linear correlation between the E_b values [134] and the σ-constants of the substituents X [135] observed for pyridine and its derivatives XC_5H_4N (Fig. 7) indicates that both the inductive and resonance effects are of considerable importance.

The reaction of the $[NO]^+[BF_4]^-$ salt with pyridine in polar solvents (MeCN, $MeNO_2$, SO_2 or sulfolane) was examined by ^1H NMR and IR spectroscopy.[136] The results obtained in the

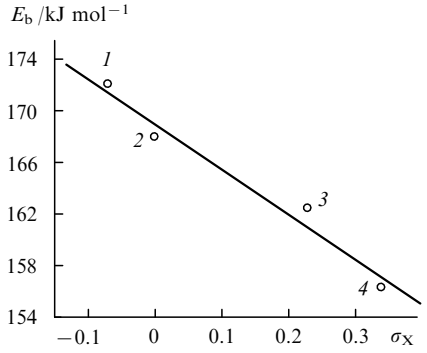
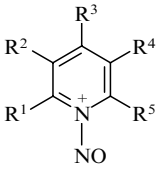


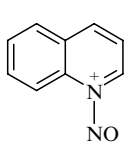
Figure 7. Correlation between the energies of binding (E_b) of the NO^+ cation with the XC_5H_4N compounds [134] and the σ-constants of the substituents X (σ_X),[135] where X = 3-Me (*1*), H (*2*), 4-Cl (*3*) or 3-F (*4*) ($r = -0.984$).

cited study provided evidence for the formation of the $C_5H_5N-NO^+$ *n*-complex (*cf.* Refs 76, 82 and 137). It should be noted that the transfer of the NO group from the nitrogen atom to the carbon atom of the ring was not observed even under the conditions of thermal decomposition of the $[C_5H_5N-NO]^+[BF_4]^-$ salt.[136]

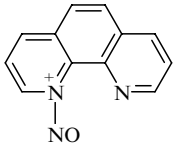
The reactions of pyridine, its derivatives, quinoline and 1,10-phenanthroline with $[NO]^+[BF_4]^-$ in $(CD_3)_2SO$ at 20 °C or with $[NO]^+[AlCl_4]^-$ in SO_2 at −60 °C afforded complexes **58a–d**, **59** and **60** whose structures were confirmed by ^1H and ^{13}C NMR spectroscopy.[138,139]



58a–d



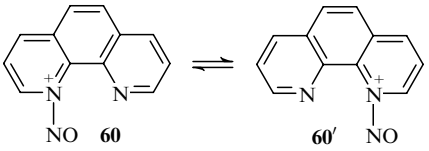
59



60

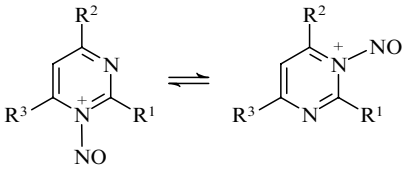
Compound **58**	R^1	R^2	R^3	R^4	R^5
a	H	H	H	H	H
b	H	Me	H	H	H
c	H	H	CHO	H	H
d	Me	H	Me	H	Me

The ^1H and ^{13}C NMR spectra of the complex **60** are indicative of a degenerate rearrangement rapid within the NMR time scale, which proceeds through the intra- and(or) intermolecular transfer of the NO group.



60 **60′**

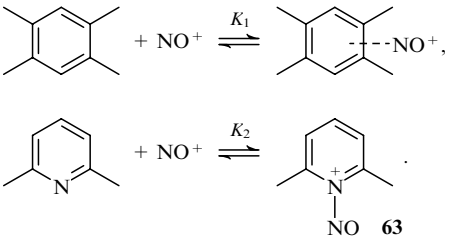
Nitrosonium complexes of pyrimidine derivatives (**61** and **62**) undergo analogous rearrangements persisting even at −70 °C.[140]



61, **62**

61: R^1 = Me, R^2 = R^3 = Ph; **62**: R^1 = PhO, R^2 = R^3 = Me.

According to the experimental data for the gas phase, pyridine derivatives and alkylbenzenes possess similar affinities for the NO^+ cation.[134] The formation constant of the 2,6-dimethylpyridine complex with the nitrosonium cation in MeCN was determined by the competitive method.[82] On gradual addition of 2,6-dimethylpyridine to a solution of the durene complex with $[NO]^+[BF_4]^-$ in acetonitrile, the intensity of the charge-transfer band for the durene–NO^+ complex decreases monotonically, while the intensity of the corresponding band for the nitrosonium complex with 2,6-dimethylpyridine increases due to the following reactions:

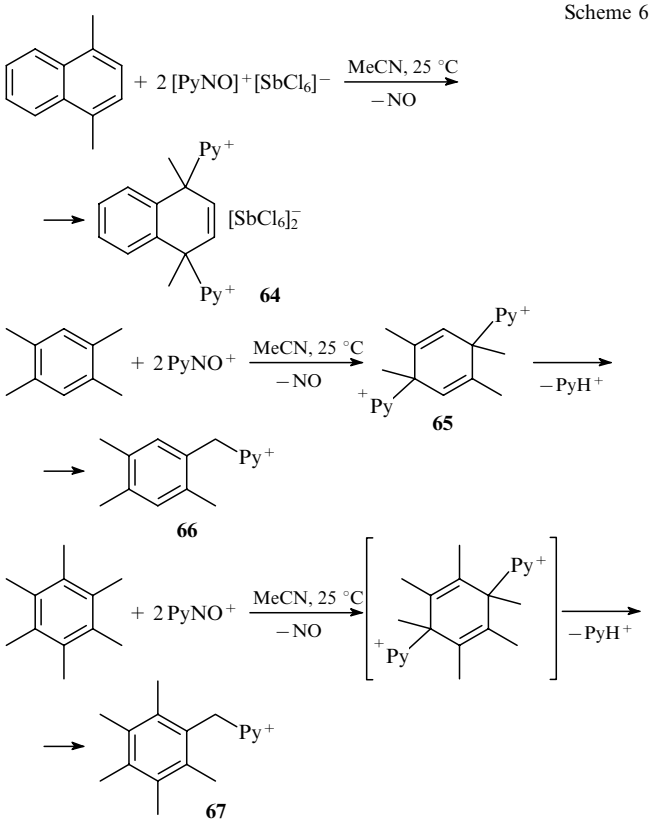


63

The equilibrium constant, K_2, of the reaction of NO^+ with 2,6-dimethylpyridine [$K_2 = (3\pm2)\times10^3$ litre mol^{-1}] was determined[82] from the equilibrium constant of the reaction of durene with the NO^+ cation (K_1 = 450 litre mol^{-1}) estimated previously. A somewhat different value was obtained for electrochemical reduction of complex **63**, ($K_2 \approx 500$ litre mol^{-1}). This difference in the constant determined by different methods is due partially to salt effects.[82]

Intensely coloured solutions of complexes of aromatic compounds with $C_5H_5N^+-NO$ ($PyNO^+$) in acetonitrile are decolourised in the presence of alkyl derivatives of benzene or naphthalene at room temperature in the dark, the rate of this process being decreased in the series 1,4-dimethylnaphthalene > hexamethylbenzene > durene ≫ *p*-xylene > toluene.[82] The chemical conversions responsible for decolouration of the complexes under the action of 1,4-dimethylnaphthalene, durene and hexamethylbenzene are shown in Scheme 6.[82]

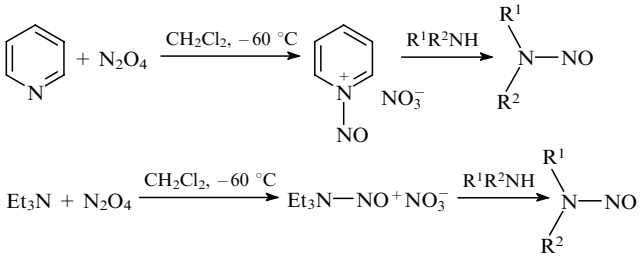
Scheme 6



64 **65** **66** **67**

The structures of complexes **64–67** were established by ^1H NMR spectroscopy. The structure of the complex **65** (with the $SbCl_6^-$ anion) was additionally confirmed by X-ray diffraction analysis. Interestingly, the reaction of durene with the $[PyNO]^+[SbCl_6]^-$ salt afforded exclusively the *trans*-adduct **65**, while the reaction with the $[PyNO]^+[BF_4]^-$ salt gave rise to an equimolar mixture of the *trans*- and *cis*-adducts.[82]

N-Nitrosation reactions of secondary amines with complexes synthesised by the reactions of N_2O_4 with pyridine or triethylamine have been examined.[137]



Analogous N-nitrosation reactions of amino acids containing secondary amine groups under the action of a mixture of nitro-

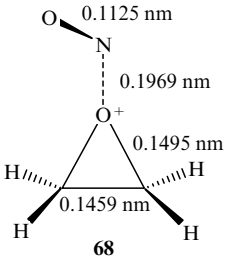
sonium tetrafluoroborate and pyridine have been described[141] (*cf.* Ref. 127). Apparently, the $[PyNO]^+[BF_4]^-$ complex served as an active nitrosating agent in these reactions.[141]

VI. Complexes of the nitrosonium ion with organic compounds containing Group VI elements

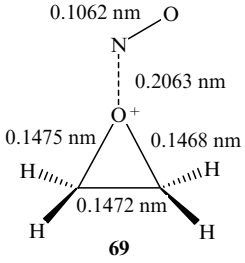
Complexes of the nitrosonium ion with compounds of the R^1ER^2 and $R^1R^2C=E$ types (E is the Group VI element) were considered as intermediates in many liquid-phase reactions of O-bases (alcohols,[1,142,143] ketones,[144–146] *etc.*[1,92–94]) and S-bases (desulfofluorination of thioesters,[147] conversions of thioketones and thioamides giving rise to ketones and amides of acids, respectively,[148] *etc.*[149–151]).

According to the results of quantum-chemical calculations[133,152–154] and experimental data for the gas phase obtained by the ion-cyclotron resonance[66,134] and kinetic methods,[134] O-bases possess rather high affinities for the NO^+ cation.

Calculations based on thermochemical data demonstrated that the energy of the nitrosonium complex with ethylene oxide (**68**) is 112.5 kJ mol^{-1} lower than those of the initial reagents.[152]

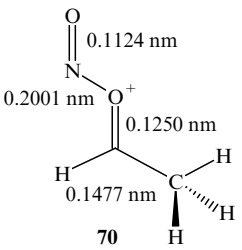


68

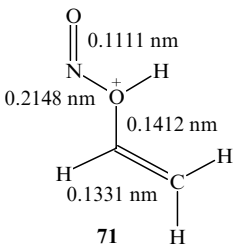


69

Ab initio calculations (SCF/MP2) demonstrated that the planar analogue of this complex (**69**) is somewhat energetically less favourable (ΔE_{rel} = 15.1 kJ mol^{-1}), the latter being a transitional structure between two equivalent forms **68**. According to the results of *ab initio* calculations (MP2/6-31+G*), the energy of the nitrosonium complex with acetaldehyde (**70**), which is isomeric with structure **68**, is 115.5 kJ mol^{-1} lower than those of the initial reagents, whereas the nitrosonium complex with the enol form of acetaldehyde (**71**) is energetically less favourable than the complex **70** (ΔE_{rel} = 105.0 kJ mol^{-1}).[152]



70



71

Analogously, *ab initio* calculations [HF/6-31+G(d)[133] and G2[154]] gave rather high affinities of the NO^+ cation for methanol (97.3 and 105.9 kJ mol^{-1}, respectively).

The *ab initio* energies of binding of the NO^+ cation with acetaldehyde and methanol are very close to the experimental values determined for the gas phase (Table 9).[134]

The energies of binding of the NO^+ cation with O-bases were analysed within the framework of Taft's equation.[66] Linear correlations were revealed for each class of compounds (MeCOR, where R = H, Me or Et; ROAc or RCHO, where R = Me, Et or Pr^i; and ROH, where R = Me, Et or Pr^i). Analogous relationships are true for the compounds of the $RONO_2$ and RNO_2 types (Fig. 8).

As mentioned above, nitrosonium complexes with O-bases were postulated for many liquid-phase reactions. However, the data on generation of these complexes in solutions are scarce.[77,155–159]

Table 9. Energies of binding (E_b) of the NO^+ cation with O-bases.[134]

Compound	E_b /kJ mol^{-1}	Compound	E_b /kJ mol^{-1}
H_2O	77.4	MeCHO	115.5
MeOH	97.5	Me_2CO	130.1
CH_2O	112.5	$MeCO_2Et$	131.4
$MeONO_2$	86.6	MeCOEt	134.3
$EtONO_2$	95.0	Et_2CO	136.8
Pr^iONO_2	101.7	Pr^iCOMe	138.1
$MeNO_2$	104.2	Bu^tCOMe	140.2
$EtNO_2$	112.5	Bu^t_2CO	141.0
Pr^nNO_2	115.9	Pr^i_2CO	142.3
Pr^iNO_2	118.0	PhCOMe	146.9
Bu^nNO_2	116.7	$(C_3H_5)_2CO$	152.7
Bu^tNO_2	123.4	Ph_2CO	160.2
$MeCOC(OMe)_2Me$	154.8	$(PhCH_2)_2CO$	165.3
$MeCO_2Bu^t$	141.0		

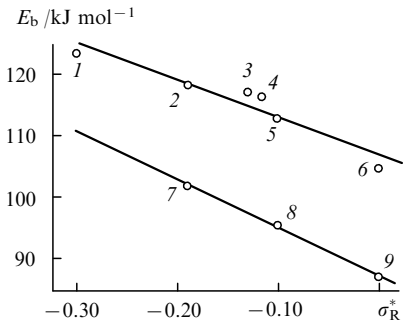


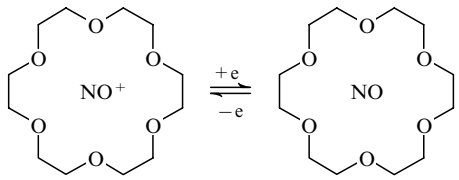
Figure 8. Correlation between the energies of binding (E_b) of the NO^+ cation with the RNO_2 (*1–6*) and $RONO_2$ compounds[134] (*7–9*) and the σ^*-constants of the substituents R (σ^*_R),[135] where R = Bu^t (*1*), Pr^i (*2*, *7*), Bu^n (*3*), Pr^n (*4*), Et (*5*, *8*) or Me (*6*, *9*) (r = −0.955 and −0.999, respectively).

Thus, the reactions of the $[NO]^+[BF_4]^-$ and $[NO]^+[PF_6]^-$ salts with 18-crown-6, 15-crown-5 and 12-crown-4 in dichloromethane, acetonitrile and nitromethane were studied by ^{1}H NMR and IR spectroscopy and conductometry.[155] The reactions of 18-crown-6 and 12-crown-4 with $[NO]^+X^-$ afforded the 1:1 and 2:1 complexes, respectively. In the case of 15-crown-5, the 1:1 stoichiometry was observed if the reaction was performed in MeCN or $MeNO_2$, whereas the 2:1 stoichiometry was achieved in CH_2Cl_2. The addition of the $[NO]^+X^-$ salt to a solution of a complex always leads to a downfield shift of the signal of the crown ether in the ^{1}H NMR spectrum, one narrow singlet being observed due to the rapid (within the NMR time scale) exchange between the free crown molecule and the molecule involved in the complex. New absorption bands at 1850–1852 and 1876 cm^{-1} appeared in the IR spectra of solutions of 18-crown-6, 15-crown-5 and 12-crown-4 in CH_2Cl_2 and MeCN, respectively, upon the addition of the $[NO]^+X^-$ salts, which indicates that the NO^+ cation is covalently bonded to the crown molecule.[155] It should be noted that the positions of the bands in the IR spectra are virtually independent of the nature of the counterion.[155]

The reaction of 18-crown-6 with the NO^+ cation (BF_4^- as the counterion) was examined by ^{1}H and ^{13}C NMR, IR and Raman spectroscopy.[156] The ^{1}H and ^{13}C NMR spectra of the 1:1 complex have singlets at δ 3.67 and 70.327, respectively. The ^{13}C chemical shift changes only slightly (by 0.428 ppm) on going from free 18-crown-6 to the ether involved in the complex. The IR spectrum of the [18-crown-6–NO]$^+[BF_4]^-$ salt (in hexachlorobutadiene) has an absorption band of the NO group at 2274 cm^{-1} the position of which differs substantially from those observed in the spectra of this complex in CH_2Cl_2 or MeCN (see above).

Analogous results were obtained in another study.[157] It was suggested that the band at 2250 cm^{-1} in the IR spectrum of a solution of the [18-crown-6–NO]$^+$[BF_4]$^-$ complex in CH_2Cl_2 and the charge-transfer band of this complex (λ_{max} = 300 nm) be used for the detection of an impurity of the [NO]$^+$[BF_4]$^-$ salt in the [NO_2]$^+$[BF_4]$^-$ specimen.[77] A polycrystalline specimen prepared by the reaction of N_2O_4 with 18-crown-6 was studied by Raman spectroscopy.[158] The Raman spectrum of the salt [18-crown-6–NO]$^+$H$^+$[NO_3^-]$_2$ has an intense band at 2270 cm^{-1} belonging to the stretching vibration of the NO^+ group bound to the crown ether. No explanation was provided for the above-mentioned differences in the stretching vibration frequency of the NO group.[156–158] Apparently, these differences are associated with a change in the mode of bonding of the NO^+ cation with 18-crown-6.

The complex of 18-crown-6 with [NO]$^+$[BF_4]$^-$ in MeCN was examined by cyclic voltammetry.[77] The complexation constant ($K > 10^4$ litre mol^{-1}) was estimated based on the oxidation and reduction potentials. Reduction of the complex **72** gave rise to the compound **73**. On oxidation of the latter, NO molecules were only partially converted into NO^+ cations and its complex with the crown ether.



72 **73**

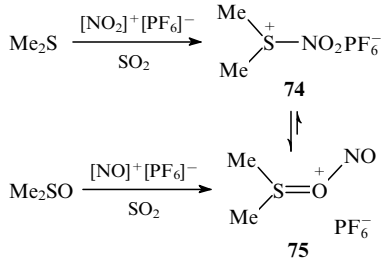
The reversible reduction potential of the complex **72** in MeCN ($E_{red} \approx 0.9$ B) is smaller than the E_{red} values determined for the hexamethylbenzene complex with the NO^+ cation (E_{red} = 1.02 V) and for NO^+ (E_{red} = 1.28 V).[77]

The reactivity of the nitrosonium cation changes substantially on the involvement of the [NO]$^+$[BF_4]$^-$ salt in the complex with 18-crown-6.[156] Thus the [18-crown-6–NO]$^+$[BF_4]$^-$ complex did not react with benzamide in MeCN at low temperature, whereas the amide was rapidly converted into acid under the action of [NO]$^+$[BF_4]$^-$ in the absence of the crown ether.[156]

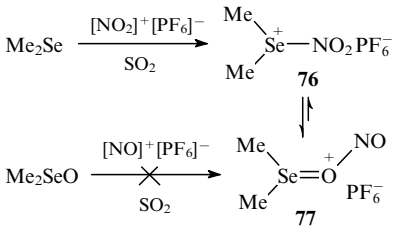
The nitrosonium cation vigorously reacts with ketones in the gas phase[66,134] to give the [R^1R^2C=ONO]$^+$ complexes (see Table 9). Analogous complexes were obtained in the reactions of the NO^+ cation with compounds of the ArN=O and R_2S=O types in the liquid phase.[93,94,159]

Kinetic studies of the mechanism of nitrosation of aromatic compounds provided evidence for the formation of [ArNO–NO]$^+$ complexes in which the nitrosonium cation is bound to the oxygen atom of the NO group in the ArNO molecule.[92–94] The formation constants of the complex of the NO^+ cation with 4-nitrosotoluene and 1,3-dimethyl-4-nitrosobenzene in trifluoroacetic acid are 58 000 and 38 000 litre mol^{-1}, respectively.[93]

Studies by ^{1}H, ^{13}C and ^{15}N NMR spectroscopy showed[159] that the reaction of [NO]$^+$[PF_6]$^-$ with dimethyl sulfoxide in SO_2 or the reaction of [NO_2]$^+$[PF_6]$^-$ with dimethyl sulfide in SO_2 at low temperature gave rise to nitrosonium complex **75** (existing in equilibrium with complex **74**).

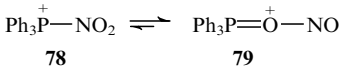


Analogously, the reaction of [NO_2]$^+$[PF_6]$^-$ with dimethyl selenide in SO_2 at −78 °C afforded nitrosonium complex **77** along with complex **76**.[159]



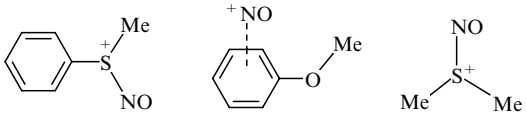
However, all attempts to generate the complex **77** by the reaction of [NO]$^+$[PF_6]$^-$ with dimethyl selenoxide failed because the latter readily underwent Pummerer fragmentation.[159]

The ambident reactivity of the NO_2^+ cation (the competitive O- or N-reactions) is manifested in its reactions with triphenylphosphine. In this case, as in the case of the S- and Se-analogues, the equilibrium **78** ⇋ **79** is shifted toward the nitritophosphonium complex **79**.[159]



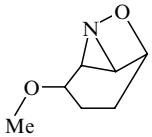
78 **79**

Investigations of the interaction of the NO^+ cation with O- and S-anions using perturbation theory demonstrated that the nitrosonium cation acts as a soft acid[160] (*cf.* Ref. 161). According to the Pearson concept,[162] the complexes of the NO^+ cation with S-bases should be more stable than those with O-bases. This statement can be exemplified by the fact that the reaction of thioanisole with [NO]$^+$[$AlCl_4$]$^-$ in the SO_2–CD_2Cl_2 system at −70 °C afforded an *n*-complex (**80**), whereas the reaction of anisole under these conditions gave rise to π-complex **81**, the oxygen atom of the anisole remaining unbound.[87]

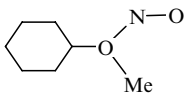


80 **81** **82**

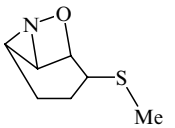
The structures of these complexes were confirmed by ^{1}H, ^{13}C and ^{15}N NMR spectroscopy. In particular, the fact that the cation **80** belongs to an *n*-complex is witnessed by the close values of the corresponding chemical shifts in the ^{15}N NMR spectra of this complex and Me_2S^+–NO (**82**) [HSO_3F–SO_2, δ(−70 °C) 291.6 and 258.6, respectively].[87] The results of quantum-chemical calculations by the MINDO/3 method confirmed that of the *n*-, π- and σ-complexes, the *n*-complex of thioanisole and the π-complex of ansiole are more stable.[87]



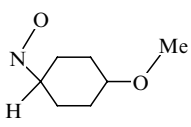
ΔH_f = 643.9 kJ mol^{-1}



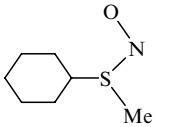
ΔH_f = 761.5 kJ mol^{-1}



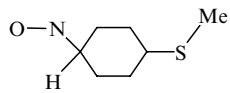
ΔH_f = 832.6 kJ mol^{-1}



ΔH_f = 663.6 kJ mol^{-1}



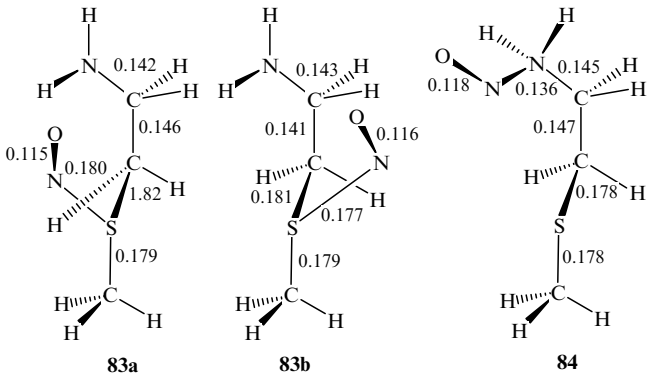
ΔH_f = 788.3 kJ mol^{-1}



ΔH_f = 854.0 kJ mol^{-1}

The preferential binding of the NO^+ cation at the sulfur atom rather than at the oxygen atom in the PhEMe compounds (E = O or S) was attributed [87] to the lower electronegativity of the S atom and a greater *p*,π-conjugation of the aromatic fragment with the MeO group compared to that with the MeS group. It was suggested [163] that binding of the nitrosonium cation in the case of thioanisole, occurs preferentially at the S atom due to the fact that the HOMO of thioanisole has the highest coefficient at the sulfur atom.

Ab initio (the 4-31G basis set), CNDO and INDO quantum-chemical calculations were performed with the aim of studying the reaction of 2-(methylthio)ethylamine with the NO^+ cation.[164] The structures of the complexes **83a**,**b** and **84** optimised by the CNDO and INDO methods are shown in Fig. 9. Analysis within the framework of perturbation theory demonstrated that the NO^+ cation acts as a soft acid, *i.e.*, it is bound primarily to the sulfur atom rather than to the nitrogen atom, the energy of the N-complex **84** being 50 kJ mol^{-1} higher than the energy of the stable *syn*-complex **83a**.[164]

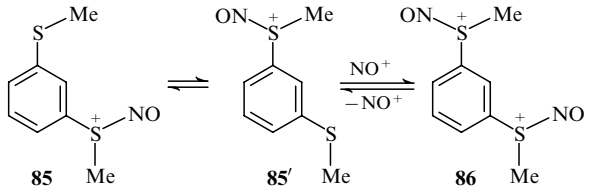


83a **83b** **84**

Figure 9. Geometric parameters of the *n*-complexes **83a**,**b** and **84** calculated by the CNDO and INDO methods.[164] The bond lengths are given in nm.

The reaction of 1,3-dimethylthiobenzene with $[NO]^+[AlCl_4]^-$ in the $SO_2-CD_2Cl_2$ system at −70 °C produced *n*-complex **85**, which underwent degenerate rearrangement, rapid within the NMR time scale (Scheme 7).[165]

Scheme 7



85 **85′** **86**

The structure of the complex **85** was confirmed by ^1H, ^{13}C and ^{15}N NMR spectroscopy. As expected, the ^{15}N chemical shift for the complex **85** (δ_N 267.1 relative to $MeNO_2$, −70 °C) is similar to that observed in the spectrum of the nitrosonium complex with thioanisole (δ_N 291.6 relative to $MeNO_2$, −70 °C).[87] The signals for the protons of the aromatic ring and methyl groups and the signals for the C(2), C(4), C(5) and C(6) atoms are shifted downfield as the 1,3-dimethylthiobenzene : $[NO]^+[AlCl_4]^-$ ratio changes from 1 : 1 to 1 : 2 due, apparently, to the shift of the equilibrium **85′** ⇌ **86** (see Scheme 7) to the dication **86**. A further increase in the amount of the salt (to 1 : 5) has no effect on the positions of the above-mentioned signals.

The complexes of dialkyl, alkylaryl and diaryl sulfides with $[NO]^+[BF_4]^-$ or N_2O_4 in CH_2Cl_2 were studied by electronic spectroscopy.[86] At low temperature, the spectra have charge-transfer bands whose positions depend only slightly on the nature of the counterion (NO_3^- or BF_4^-) (Table 10). It was demonstrated

Table 10. Parameters of electronic absorption spectra (λ_{CT} /nm) of the nitrosonium complexes with the R^1R^2E compounds (E = S or Se) in CH_2Cl_2 at −78 °C.[86, 166]

R^1	R^2	λ_{CT} (E = S)		λ_{CT} (E = Se)	
		A	B	A	B
Me	Me	390	393	–	–
Bu^n	Bu^n	400	400	–	–
Me	$PhCH_2$	406	406	426	424
Me	Bu^t	396	400	–	–
$(CH_2)_4$		387	386	–	–
Bu^t	$Me(CH_2)_{17}$	–	408	–	–
Me	Ph	502	500	494	498
Et	Ph	500	500	–	–
Pr^i	Ph	494	494	500	496
Me	*p*-ClC_6H_4	510	512	–	–
Me	*p*-MeC_6H_4	514	514	–	–
Me	*p*-$MeOC_6H_4$	542	542	–	–
Me	*p*-$Bu^tC_6H_4$	514	517	–	–
$PhCH_2$	$PhCH_2$	–	–	452	444
Ph	$PhCH_2$	506	–	508	506
Ph	Ph	558	563	–	–

Note. A and B are the complexes with the $[NO]^+[BF_4]^-$ salt and N_2O_4, respectively.

that low-temperature irradiation of the $[R^1R^2SNO]^+[NO_3]^-$ complexes at the frequency corresponding to the charge-transfer band afforded sulfoxides. The complexation constants for dialkyl and alkylaryl sulfides (K_1 and K_2, respectively) were estimated by the competitive method.

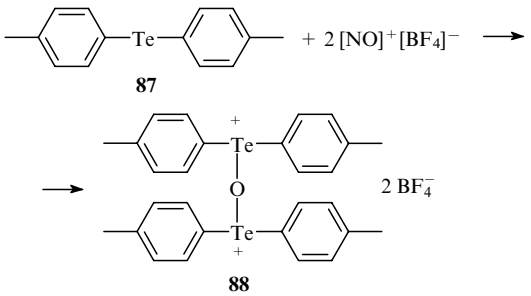
$$R_2S + [NO]^+[BF_4]^- \overset{K_1}{\rightleftharpoons} [R_2S, NO]^+[BF_4]^-$$

$$R_2S + [ArH, NO]^+[BF_4]^- \overset{K_2}{\rightleftharpoons} [R_2S, NO]^+[BF_4]^- + ArH$$

The complexation constant (K_1) for Bu^n_2S in CH_2Cl_2 at −78 °C is similar to that for hexamethylbenzene ($K_1 \approx 3 \times 10^4$ litre mol^{-1}), whereas ethylphenyl sulfide possesses a somewhat lower affinity for the NO^+ cation ($K_1 \leqslant 3 \times 10^3$ litre mol^{-1}).

Analogously, the reactions of dialkyl and alkylaryl selenides with $[NO]^+[BF_4]^-$ or N_2O_4 in CH_2Cl_2 at −78 °C gave rise to the nitrosonium complexes $R^1R^2SeNO^+$ (see Table 10).[166] As can be seen from Table 10, the positions of charge-transfer bands in the spectra of the nitrosonium complexes R^1R^2S and R^1R^2Se are rather close. Low-temperature irradiation of the complex $[PhMeSeNO]^+[NO_3]^-$ at the frequency ν_{CT} gave rise to the corresponding selenoxide PhSe(O)Me.[166]

The reactions of nitrosonium salts with diaryl tellurides, unlike those with S- and Se-containing aromatic compounds, did not produce nitrosonium complexes.[167] Thus treatment of bis(4-methylphenyl) telluride (**87**) with the $[NO]^+[BF_4]^-$ salt in the CH_2Cl_2-MeCN system at −40 °C under an atmosphere of argon afforded dication **88**.

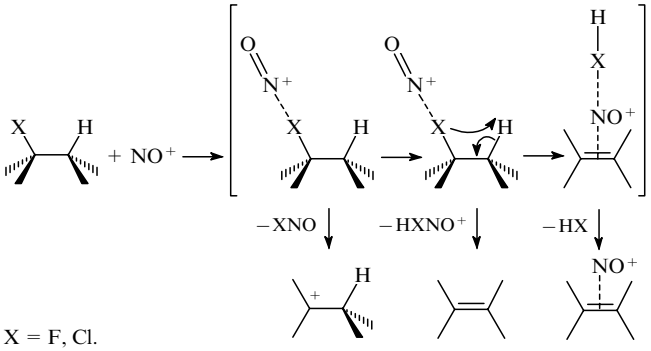


87 **88**

It was found that the oxygen atom in the dication **88** was derived from the nitrosonium salt.[167]

VII. Complexes of the nitrosonium ion with halogen-containing organic compounds

The reactions of the nitrosonium cation with organic halogen derivatives RX in the gas phase generate chemically active species, which can dissociate to form carbocations, nitrosyl halides and nitrosonium complexes of alkenes.[168]



X = F, Cl.

The latter react with alkyl halides yielding halonitrosonium complexes. Thus the reactions involving Pr^iCl or Pr^iF proceeded as follows:[168]

$$(MeCH{=}CH_2)\cdot NO^+ + Pr^iX \longrightarrow Pr^iX\cdot NO^+ + C_3H_6$$

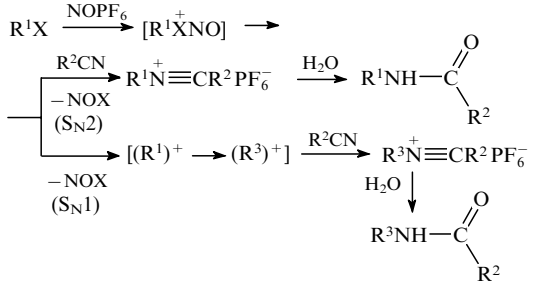
X = F, Cl.

It is assumed that analogous ion-molecular reactions take place upon interaction of the vibrationally excited NO^+ cation with different alkyl halides (see Ref. 169 and references cited therein).

The data on the energies of binding of the NO^+ cation with alkyl chlorides RCl (R = Me, Et or Pr^i; E_b = 77.4, 82.0 and 89.5 kJ mol^{-1}, respectively) were determined by the ion-cyclotron resonance and kinetic methods.[134] The following correlation between the E_b values for aryl chlorides and Taft's σ^*-constants was deduced: [135]

$$E_b = (76.8 \pm 1.3) - (63.4 \pm 10.7)\,\sigma^*,\ r = -0.986,\ s = 1.4.$$

To our knowledge, the data on generation of long-lived nitrosonium complexes of halogen-containing organic compounds in solutions are lacking. However, such complexes can be generated in different reactions of alkyl and aryl halides with salts of the nitrosonium cation.[170, 171] Thus, a new procedure was developed [170] for the preparation of amides by the reactions of alkyl or aryl halides with nitriles in the presence of the $[NO]^+X^-$ salts. The assumed mechanism involves the formation of a nitrosonium *n*-complex *via* the lone electron pairs of the halogen atom followed by nucleophilic substitution (of the S_N1 or S_N2 type) of nitrile for the XNO^+ group.[170]



R^1 = Alk, $ArCR^2R^3$; R^2 = Me, Et, Pr, Ph, $PhCH_2$;
$(R^3)^+$ — isomer $(R^1)^+$; X = F, Cl, Br.

Analogous results were obtained in another study. [172]

* * *

To summarise, abundant data on the structures and reactivities of different classes of nitrosonium organic complexes have been accumulated due to the extensive use of modern physical and quantum-chemical methods. In the present review, we generalise the results of recent studies in this area. The necessity of summarising these data stems from the fact that investigations aimed at refining the theoretical notion of the processes, which involve nitrosonium complexes and include both classical organic and biochemical reactions, are progressing rapidly.

This review has been written with the financial support of the Russian Foundation for Basic Research (Project No. 99–03–32878).

References

1. D L H Williams *Nitrosation* (Cambridge: Cambridge University Press, 1988)
2. P P Kadzyauskas, N S Zefirov *Usp. Khim.* **37** 1243 (1968) [*Russ. Chem. Rev.* **37** 543 (1968)]
3. P B D de la Mare, R Bolton *Electrophilic Additions to Unsaturated Systems* (Amsterdam: Elsevier, 1982) p. 247
4. L F Fieser, M Fieser *Reagents for Organic Synthesis* (New York: Wiley, 1968)
5. G A Olah, K K Laali, Q Wang, G K S Prakash, in *Onium Ions* (New York: Wiley, 1998) p. 40
6. E Culotta, D E Koshland *Science* **258** 1862 (1992)
7. A R Butler, D L H Williams *Chem. Soc. Rev.* **22** 233 (1993)
8. M Fontecave, J-L Pierre *Bull. Soc. Chim. Fr.* **131** 620 (1994)
9. V P Reutov, in *Uspekhi Biologicheskoi Khimii* (Advances in Biological Chemistry) (Ed. B F Poglazov) (Pushchino: Izd. ONTI PNTs RAN, 1995) Vol. 35, p. 189
10. A R Butler *Chem. Ind.* 828 (1995)
11. J S Stamler, M Feelisch, in *Methods in Nitric Oxide Research* (Eds M Feelisch, J S Stamler) (Chichester: Wiley, 1996) p. 19
12. F Murad *Angew. Chem., Int. Ed. Engl.* **38** 1856 (1999)
13. R F Furchgott *Angew. Chem., Int. Ed. Engl.,* **38** 1870 (1999)
14. L J Ignarro *Angew. Chem., Int. Ed. Engl.* **38** 1882 (1999)
15. R P Patel, J McAndrew, H Sellak, C R White, H Jo, B A Freeman, V M Darley-Usmar *Biochim. Biophys. Acta* **1411** 385 (1999)
16. S A Lipton, Y-B Choi, Z-H Pan, S Z Lei, H-S V Chen, N J Sucher, J Loscalzo, D J Singel, J S Stamler *Nature (London)* **364** 626 (1993)
17. J S Stamler, D J Singel, J Loscalzo *Science* **258** 1898 (1992)
18. A R Butler, F W Flitney, D L H Williams *Trends Pharmacol. Sci.* **16** 18 (1995)
19. M A de Groote, T Testerman, Y Xu, G Stauffer, F C Fang *Science* **272** 414 (1996)
20. M N Hughes *Biochim. Biophys. Acta* **1411** 263 (1999)
21. J J Kirchner, S T Sigurdsson, P B Hopkins *J. Am. Chem. Soc.* **114** 4021 (1992)
22. A H Elcock, P D Lyne, A J Mulholland, A Nandra, W G Richards *J. Am. Chem. Soc.* **117** 4706 (1995)
23. P Mack, J M Dyke, T G Wright *Chem. Phys.,* **218** 243 (1997)
24. L Angel, A J Stace *J. Phys. Chem., A* **102** 3037 (1998)
25. G A Olah, O Farooq, G K S Prakash, in *Activation and Functionalization of Alkanes* (Ed. C L Hill) (New York: Wiley, 1989) p. 27
26. G A Olah, G K S Prakash, R E Williams, L D Field, K Wade *Hypercarbon Chemistry* (New York: Wiley-Interscience, 1987)
27. G A Olah, G K S Prakash, J Sommer *Superacids* (New York: Wiley-Interscience, 1985)
28. G A Olah, J G Shih, B P Singh, B G B Gupta *J. Org. Chem.* **48** 3356 (1983)
29. G A Olah, P Ramaiah, C B Rao, G Sandford, R Golam, N O Trivedi, J A Olah *J. Am. Chem. Soc.* **115** 7246 (1993)
30. G A Olah, B G B Gupta *J. Org. Chem.* **45** 3532 (1980)
31. A A Fokin, P A Gunchenko, S A Peleshanko, P von R Schleyer, P R Schreiner *Eur. J. Org. Chem.* 855 (1999)
32. P R Schreiner, P von R Schleyer, H F Schaefer III *J. Am. Chem. Soc.* **115** 9659 (1993)
33. P R Schreiner, P von R Schleyer, H F Schaefer III *J. Am. Chem. Soc.* **117** 453 (1995)
34. M L Scheinbaum, M B Dines *Tetrahedron Lett.* 2205 (1971)
35. G H Lee, J M Lee, W B Jeong, K Kim *Tetrahedron Lett.* **29** 4437 (1988)
36. R L Danheiser, D A Becker *Heterocycles* **25** 277 (1987)

37. H O Bertrand, J L Burgot *Phosphorus Sulfur Silicon Relat. Elem.* **97** 103 (1994)
38. A V Pankratov *Khimiya Ftoridov Azota* (The Chemistry of Nitrogen Fluorides) (Moscow: Khimiya, 1973)
39. Q B Broxterman, H Hogeveen, R F Kingma, F van Bolhuis *J. Am. Chem. Soc.* **107** 5722 (1985)
40. G A Olah, G Salem, J S Staral, T-L Ho *J. Org. Chem.* **43** 173 (1978)
41. V S Savostin, I I Krylov, A P Kutepov, A I Rapkin, A V Fokin *Izv. Akad. Nauk SSSR, Ser. Khim.* 1851 (1990) [a]
42. R Chang, K Kim *Bull. Korean Chem. Soc.* **16** 475 (1995)
43. R M Minyaev, M E Kletskii, V I Minkin *Zh. Org. Khim.* **23** 2508 (1987) [b]
44. K Raghavachari, W D Reents, Jr, R C Haddon *J. Comput. Chem.* **7** 265 (1986)
45. V I Minkin, I A Yudilevich, R M Minyaev *Zh. Org. Khim.* **23** 717 (1987) [b]
46. M N Glukhovtsev, P von R Schleyer, N J R von E Hommes, V I Minkin *Chem. Phys. Lett.* **205** 529 (1993)
47. G A Olah, P Schilling, P W Westerman, H C Lin *J. Am. Chem. Soc.* **96** 3581 (1974)
48. G I Borodkin, I R Elanov, V A Podryvanov, M M Shakirov, V G Shubin *J. Am. Chem. Soc.* **117** 12863 (1995)
49. G I Borodkin, I R Elanov, M M Shakirov, V G Shubin *Zh. Org. Khim.* **33** 363 (1997) [b]
50. G I Borodkin, I R Elanov, A M Genaev, M M Shakirov, V G Shubin *Mendeleev Commun.* 83 (1999)
51. E Bosch, J K Kochi *Res. Chem. Intermed.* **22** 209 (1996)
52. F Blatter, H Frei *J. Phys. Chem.* **97** 1178 (1993)
53. R Rathore, S V Lindeman, J K Kochi *Angew. Chem., Int. Ed. Engl.* **37** 1585 (1998)
54. S Sankararaman, W Lau, J K Kochi *J. Chem. Soc., Chem. Commun.* 396 (1991)
55. J K Kochi *Acta Chem. Scand.* **44** 409 (1990)
56. J K Kochi *Acc. Chem. Res.* **25** 39 (1992)
57. G I Borodkin, V G Shubin *Zh. Org. Khim.* **36** 479 (2000) [b]
58. D Dimitrov, F Fratev *Compt. Rend. Acad. Bulg. Sci.* **16** 729 (1963)
59. D Dimitrov, F Fratev *Compt. Rend. Acad. Bulg. Sci.* **16** 825 (1963)
60. Z J Allan, J Podstata, D Šnobl, J Jarkovský *Tetrahedron Lett.* 3565 (1965)
61. Z J Allan, J Podstata, D Šnobl, J Jarkovský *Collect. Czech. Chem. Commun.* **32** 1449 (1967)
62. E Hunziker, J R Penton, H Zollinger *Helv. Chim. Acta* **54** 2043 (1971)
63. A R Butler, A P Sanderson *J. Chem. Soc., Perkin Trans. 2* 1671 (1974)
64. W D Reents Jr, B S Freiser *J. Am. Chem. Soc.* **102** 271 (1980)
65. R Wolfschütz, H Schwarz. *Int. J. Mass Spectrom. Ion Phys.* **33** 291 (1980)
66. W D Reents Jr, B S Freiser *J. Am. Chem. Soc.* **103** 2791 (1981)
67. J A Stone, D E Splinter, S Y Kong *Can. J. Chem.* **60** 910 (1982)
68. V I Mamatyuk, A N Detsina, Sh M Nagi, Yu V Gatilov, G I Borodkin, I L Mudrakovskii, in *III Vsesoyuz. Soveshch. 'Spektroskopiya Koordinatsionnykh Soedinenii' (Tez. Dokl.), Krasnodar, 1984* [The IIIth All-Union Meeting 'Spectroscopy of Coordination Compounds' (Abstracts of Reports), Krasnodar, 1984] p. 55
69. S Brownstein, E Gabe, F Lee, L Tan *J. Chem. Soc., Chem. Commun.* 1566 (1984)
70. V I Minkin, R M Minyaev, I A Yudilevich, M E Kletskii *Zh. Org. Khim.* **21** 926 (1985) [b]
71. G I Borodkin, Sh M Nagi, Yu V Gatilov, V I Mamatyuk, I L Mudrakovskii, V G Shubin *Dokl. Akad. Nauk SSSR* **288** 1364 (1986) [c]
72. S Brownstein, A Morrison, L K Tan *Can. J. Chem.* **64** 265 (1986)
73. S Brownstein, E Gabe, F Lee, A Piotrowski *Can. J. Chem.* **64** 1661 (1986)
74. S Brownstein, E Gabe, B Irish, F Lee, B Louie, A Piotrowski *Can. J. Chem.* **65** 445 (1987)
75. A E Mefed, Sh M Nagi, G I Borodkin, V I Mamatyuk, V G Shubin *Dokl. Akad. Nauk SSSR* **297** 133 (1987) [c]
76. E K Kim, J K Kochi *J. Org. Chem.* **54** 1692 (1989)
77. K Y Lee, D J Kuchynka, J K Kochi *Inorg. Chem.* **29** 4196 (1990)
78. E K Kim, J K Kochi *J. Am. Chem. Soc.* **113** 4962 (1991)
79. T M Bockman, Z J Karpinski, S Sankararaman, J K Kochi *J. Am. Chem. Soc.* **114** 1970 (1992)
80. G I Borodkin, I R Elanov, M M Shakirov, V G Shubin *Izv. Akad. Nauk, Ser. Khim.* 2104 (1992) [a]
81. E K Kim, J K Kochi *J. Org. Chem.* **58** 786 (1993)
82. K Y Lee, J K Kochi *J. Chem. Soc., Perkin Trans. 2* 237 (1994)
83. E Bosch, J K Kochi *J. Org. Chem.* **59** 3314 (1994)
84. E Bosch, J K Kochi *J. Org. Chem.* **59** 5573 (1994)
85. R Rathore, E Bosch, J K Kochi *Tetrahedron* **50** 6727 (1994)
86. E Bosch, J K Kochi *J. Org. Chem.* **60** 3172 (1995)
87. G I Borodkin, V A Podryvanov, M M Shakirov, V G Shubin *J. Chem. Soc., Perkin Trans. 2* 1029 (1995)
88. R Rathore, S V Lindeman, J K Kochi *J. Am. Chem. Soc.* **119** 9393 (1997)
89. S Skokov, R A Wheeler *J. Phys. Chem. A,* **103** 4261 (1999)
90. S M Hubig, J K Kochi *J. Am. Chem. Soc.* **122** 8279 (2000)
91. A R Butler, A P Sanderson *J. Chem. Soc., Perkin Trans. 2* 989 (1972)
92. V L Lobachev, O B Savsunenko, E S Rudakov *Kinet. Katal.* **32** 17 (1991) [d]
93. J H Atherton, R B Moodie, D R Noble *J. Chem. Soc., Perkin Trans. 2* 699 (1999)
94. J H Atherton, R B Moodie, D R Noble *J. Chem. Soc., Perkin Trans. 2* 229 (2000)
95. M V Gorelik, V I Lomzakova, E A Khamidova, V Ya Shteiman, M G Kuznetsova *Zh. Org. Khim.* **31** 408 (1995) [b]
96. L R Dix, R B Moodie *J. Chem. Soc., Perkin Trans. 2* 1097 (1986)
97. M V Gorelik, V I Lomzakova, E A Khamidova, V Ya Shteiman, M G Kuznetsova, A M Andrievskii *Zh. Org. Khim.* **31** 553 (1995) [b]
98. D J Mills, J H Ridd *J. Chem. Soc., Perkin Trans. 2* 637 (1980)
99. V I Minkin, R M Minyaev *Zh. Org. Khim.* **15** 1569 (1979) [b]
100. R M Minyaev *Zh. Org. Khim.* **20** 897 (1984) [b]
101. V I Minkin, R M Minyaev *Neklassicheskie Struktury Organicheskikh Soedinenii* (Non-classical Structures of Organic Compounds) (Rostov-on-Don: Rostov State University, 1985)
102. J B Stothers *Carbon-13 NMR Spectroscopy* (New York: Academic Press, 1972)
103. V A Koptyug *Arenonievye Iony. Stroenie i Reaktsionnaya Sposobnost'* (Arenonium Ions. Structure and Reactivity) (Novosibirsk: Nauka, 1983)
104. V I Minkin, B Ya Simkin, R M Minyaev *Kvantovaya Khimiya Organicheskikh Soedinenii. Mekhanizmy Reaktsii* (Quantum Chemistry of Organic Compounds. Mechanisms of Reactions) (Moscow: Khimiya, 1986)
105. R Rathore, J K Kochi *J. Org. Chem.* **63** 8630 (1998)
106. V F Loktev, V G Shubin *Izv. Akad. Nauk SSSR, Ser. Khim.* 2276 (1987) [a]
107. G I Borodkin, I R Elanov, V G Shubin, in *Book of Abstracts of the 13th IUPAC Conference on Physical Organic Chemistry, Inchon, 1996* p. 243
108. L Eberson, F Radner *Acc. Chem. Res.* **20** 53 (1987)
109. A S Morkovnik *Usp. Khim.* **57** 254 (1988) [*Russ. Chem. Rev.* **57** 144 (1988)]
110. V N Kondrat'ev (Ed.) *Energii Razryva Khimicheskikh Svyazei. Potentsialy Ionizatsii i Srodstvo k Elektronu* (Energies of Rupture of Chemical Bonds. Ionisation Potentials and Electron Affinities) (Moscow: Nauka, 1974)
111. A S Morkovnik, O Yu Okhlobystin *Zh. Obshch. Khim.* **55** 692 (1985) [e]
112. A S Morkovnik, N M Dobaeva, O Yu Okhlobystin *Zh. Obshch. Khim.* **59** 921 (1989) [e]
113. G I Borodkin, I R Elanov, V G Shubin, in *Sovremennye Problemy Organicheskogo Sinteza (Tez. Dokl. Vsesoyuz. Konf. Molodykh Uchenykh), Irkutsk, 1988* [Topical Problems of Organic Synthesis (Abstracts of Reports of The All-Union Conference of Young Scientists), Irkutsk, 1988] p. 141
114. G I Borodkin, I R Elanov, M M Shakirov, V G Shubin, in *Tez. Dokl. Chetvertoi Vsesoyuz. Konf. po Khimii Nizkikh Temperatur, Moskva, 1988* (Abstracts of Reports of the Fourth All-Union Conference on the Chemistry of Low Temperatures, Moscow, 1988) p. 119
115. G I Borodkin, I R Elanov, M M Shakirov, V G Shubin *Izv. Akad. Nauk SSSR, Ser. Khim.* 206 (1989) [a]
116. G I Borodkin, I R Elanov, M M Shakirov, V G Shubin *J. Phys. Org. Chem.* **6** 153 (1993)

117. G I Borodkin, I R Elanov, M M Shakirov, V G Shubin *Zh. Org. Khim.* **27** 889 (1991) [b]
118. G I Borodkin, I R Elanov, P-C Cheng, L T Scott, V G Shubin, in *Book of Abstracts of the Sixth European Symposium on Organic Reactivity, Louvain-la-Neuve, 1997* p. 98
119. G I Borodkin, E I Chernyak, M M Shakirov, V G Shubin *Zh. Org. Khim.* **26** 785 (1990) [b]
120. N V Vasil'eva, V F Starichenko, V A Koptyug *Zh. Org. Khim.* **23** 1020 (1987) [b]
121. F Radner *J. Org. Chem.* **53** 702 (1988)
122. M Tanaka, H Nakashima, M Fujiwara, H Ando, Y Souma *J. Org. Chem.* **61** 788 (1996)
123. A Castro, E Iglesias, J R Leis, M E Peña, J V Tato, D L H Williams *J. Chem. Soc., Perkin Trans. 2* 1165 (1986)
124. R N Loeppky, W Cui *Tetrahedron Lett.* **39** 1845 (1998)
125. R N Loeppky, Y T Bao, J Bae, L Yu, G Shevlin, in *Nitrosamines and Related N-Nitroso Compounds. Chemistry and Biochemistry* (Eds R N Loeppky, C J Michejda) (Washington, DC: American Chemical Society, 1994) p. 52
126. D L H Williams, in *Nitrosamines and Related N-Nitroso Compounds. Chemistry and Biochemistry* (Eds R N Loeppky, C J Michejda) (Washington, DC: American Chemical Society, 1994) p. 66
127. M A Freitas, R A J O'Hair, J A R Schmidt, S E Tichy, B E Plashko, T D Williams *J. Mass Spectrom.* **31** 1086 (1996)
128. A S Morkovnik, L N Divaeva, O Yu Okhlobystin *Zh. Obshch. Khim.* **58** 2174 (1988) [e]
129. C York, G K S Prakash, Q Wang, G A Olah *Synlett* 425 (1994)
130. H Cai, J C Fishbein *J. Am. Chem. Soc.* **121** 1826 (1999)
131. S A Kulkarni, S S Pundlik *Chem. Phys. Lett.* **245** 143 (1995)
132. M Aschi, F Grandinetti *Chem. Phys. Lett.* **267** 98 (1997)
133. L L Torday, M B Santillán, G M Ciuffo, E A Jáuregui, J Pataricza, J G Papp, I G Csizmadia *J. Mol. Struct. (Theochem)* **465** 69 (1999)
134. F Cacace, G de Petris, F Pepi *Proc. Natl. Acad. Sci. USA* **94** 3507 (1997)
135. Yu A Zhdanov, V I Minkin *Korrelyatsionnyi Analiz v Organicheskoi Khimii* (Correlation Analysis in Organic Chemistry) (Rostov-on-Don: Rostov State University, 1966)
136. G A Olah, J A Olah, N A Overchuk *J. Org. Chem.* **30** 3373 (1965)
137. N N Makhova, G A Karpov, A N Mikhailyuk, A E Bova, L I Khmel'nitskii, S S Novikov *Izv. Akad. Nauk SSSR, Ser. Khim.* 226 (1978) [a]
138. G I Borodkin, V G Shubin, R V Andreev, in *Book of Abstracts of the International Conference on Reactive Intermediates and Reaction Mechanisms, Ascona, 1998* p. 38
139. R V Andreev, G I Borodkin, V G Shubin, in *Molodezhnaya Nauchnaya Shkola po Organicheskoi Khimii (Tez. Dokl.), Ekaterinburg, 1999* [Young Researchers' School on Organic Chemistry (Abstracts of Reports), Ekaterinburg, 1999] p. 65
140. G I Borodkin, R V Andreev, I R Elanov, V G Shubin, in *Book of Abstracts of the 7th European Symposium on Organic Reactivity, Ulm, 1999* p. 136
141. H T Nagasawa, P S Fraser, D L Yuzon *J. Med. Chem.* **16** 583 (1973)
142. M J Crookes, D L H Williams *J. Chem. Soc., Chem. Commun.* 571 (1988)
143. G A Olah, P Ramaiah *J. Org. Chem.* **58** 4639 (1993)
144. J R Leis, M E Peña, D L H Williams *J. Chem. Soc., Chem. Commun.* 45 (1987)
145. J R Leis, M E Peña, D L H Williams, S D Mawson *J. Chem. Soc., Perkin Trans. 2* 157 (1988)
146. A Castro, M González, F Meijide, M Mosquera *J. Chem. Soc., Perkin Trans. 2* 2021 (1988)
147. C York, G K S Prakash, G A Olah *Tetrahedron* **52** 9 (1996)
148. G A Olah, M Arvanaghi, L Onannesian, G K S Prakash *Synthesis* 785 (1984)
149. Y L Chow, K Iwai *J. Chem. Soc., Perkin Trans. 2* 931 (1980)
150. F Meijide, G Stedman *J. Chem. Soc., Perkin Trans. 2* 1087 (1988)
151. A Coello, F Meijide, J V Tato *J. Chem. Soc., Perkin Trans. 2* 1677 (1989)
152. F Cacace, G de Petris, F Pepi, I Rossi, A Venturini *J. Am. Chem. Soc.* **118** 12 719 (1996)
153. F Bernardi, M A Robb, I Rossi, A Venturini *J. Org. Chem.* **58** 7074 (1993)
154. M Aschi, F Grandinetti *Chem. Phys. Lett.* **258** 123 (1996)
155. G S Heo, P E Hillman, R A Bartsch *J. Heterocycl. Chem.* **19** 1099 (1982)
156. R Savoie, M Pigeon-Gosselin, A Rodrigue, R Chênevert *Can. J. Chem.* **61** 1248 (1983)
157. R L Elsenbaumer *J. Org. Chem.* **53** 437 (1988)
158. S Ricard, P Audet, R Savoie *J. Mol. Struct.*, **178** 135 (1988)
159. G A Olah, B G B Gupta, S C Narang *J. Am. Chem. Soc.* **101** 5317 (1979)
160. K A Jørgensen, M T M El-Wassimy, S-O Lawesson *Acta Chem. Scand., Ser. B* **37** 785 (1983)
161. K A Jørgensen, S-O Lawesson *J. Chem. Soc., Perkin Trans. 2* 231 (1985)
162. R G Pearson *Symmetry Rules for Chemical Reactions. Orbital Topology and Elementary Processes* (New York: Wiley, 1976)
163. O Dolgounitcheva, V G Zakrzewski, J V Ortiz, G V Ratovski *Int. J. Quantum Chem.* **70** 1037 (1998)
164. K A Jørgensen *J. Org. Chem.* **50** 4758 (1985)
165. G I Borodkin, E B Belikova, M M Shakirov, V G Shubin *Zh. Org. Khim.* **34** 1868 (1998) [b]
166. E Bosch, J K Kochi *J. Chem. Soc., Perkin Trans. 1* 2731 (1996)
167. K Kobayashi, N Deguchi, E Horn, N Furukawa *Angew. Chem., Int. Ed. Engl.* **37** 984 (1998)
168. A D Williamson, J L Beauchamp *J. Am. Chem. Soc.* **97** 5714 (1975)
169. T Wyttenbach, M T Bowers *J. Phys. Chem.* **96** 8920 (1992)
170. G A Olah, B G B Gupta, S C Narang *Synthesis* 274 (1979)
171. C Matt, A Wagner, C Mioskowski *J. Org. Chem.* **62** 234 (1997)
172. R D Bach, T H Taaffee, S J Rajan *J. Org. Chem.* **45** 165 (1980)

[a] — *Russ. Chem. Bull. (Engl. Transl.)*
[b] — *Russ. J. Org. Chem. (Engl. Transl.)*
[c] — *Dokl. Chem. Technol., Dokl. Chem. (Engl. Transl.)*
[d] — *Kinet. Catal. (Engl. Transl.)*
[e] — *Russ. J. Gen. Chem. (Engl. Transl.)*