Quantum chemical analysis of coordination of nitroxide probes to acid sites on the surfaces of oxides

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Abstract

Quantum chemical analysis of coordination of nitroxides on the surfaces of alumina, gallia, and silica is performed. Structural, magnetic resonance and energy characteristics of coordination are calculated. Different cluster models of the surface acid sites (AS) are tested. The results of ESR experiments are interpreted. The comparison of Lewis acid sites (LAS) of alumina and gallia surfaces is carried out. Different ways of coordination of nitroxides with two electron-donating groups are analyzed. © 2001 Elsevier Science B.V. All rights reserved.

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1. Introduction

Catalytic activity of many oxide systems is caused by proton and Lewis acid sites (LAS) on their surfaces. The structure and properties of surface acid sites (AS) can be effectively investigated by method of paramagnetic complexes of probe molecules. Stable nitroxides are commonly used as convenient and informative probes. These radicals form paramagnetic surface complexes (PSC) with active AS of oxides. ESR investigations of such complexes provide valuable information about the structure, strength, and number of catalytically active AS [1–4].

The information content of ESR spectra can be markedly increased by quantum chemical analysis of a number of physicochemical parameters of PSC [5–8]. Therefore, we have performed quantum chemical calculations of structural, radiospectroscopic, and energy characteristics of the coordination of various nitroxides on the surfaces of some oxide catalysts.

The most frequently used nitroxide is 2,2,6,6-tetramethylpiperidin-*N*-oxyl (TEMPO) (**1**) (see Fig. 1). The interest in the use of stable nitroxides of the imidazoline and imidazolidine series (**2–5**) recently increased [3,4,9]. These radicals possess two electron-donating centers (paramagnetic N–O group and N(3) atom of five-membered imidazoline or imidazolidine ring), which compete for the formation of PSC on oxide systems. Moreover, these radicals can coordinate by both electron-donating centers. Analyzing such complexes by quantum chemical methods, it is possible to obtain more detailed information about the distribution of catalytically active AS on the surfaces of oxides.

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3: X=CH$_3$
4: X=Ph
5: X=C$_8$H$_{17}$

1   **2**

Fig. 1. TEMPO and nitroxides of imidazolidine and imidazoline series.

2. The scheme of cluster quantum chemical analysis

Proceeding with quantum chemical analysis of the coordination of nitroxide probes on the surfaces of oxide catalysts, it is important above all to choose adequate models of their surface AS. It is readily effected by handling the widely distributed cluster approximation [10]. This approach consists in cutting out of an imperfect crystal, a limited structural fragment (cluster) containing comparatively a small number of atoms and representing the chemical essence of an active surface site. In doing so, the artificial free valences inevitably spring up on the cluster boundary. Most commonly, these valences are either forcedly saturated with H atoms (if creating a covalent cluster model composed of atoms is possible) or annihilated due to elaborating a so-called uncharged cluster shareholder made up of normal ions and boundary pseudo-ions [11].

The coordination of nitroxide probes on the surfaces of alumina, gallia, and silica falls into a group of the most-properly studied to date. On the ground of radiospectroscopy data, the strongest LAS on the surfaces of alumina or gallia are thought in general to be truncated tetrahedra, containing three-coordinated ions Al^{3+} and Ga^{3+}. The preferred existence of such LAS on the surfaces of dehydroxylated alumina and gallia follows also from the observation that the magnetic resonance parameters (g-tensors and hyperfine coupling constants) of the resulting PSC are very close to those obtained by ESR technique for analogous complexes of nitroxides with corresponding trichlorides in nonpolar solvents [12]. Therefore, the simplest covalent cluster models of the LAS under discussion are saturated with H atoms structural fragments of the

surfaces of alumina and gallia (Al(OH)$_3$ or Ga(OH)$_3$ correspondingly).

It is well known that silanol groups are typical adsorption centers on the silica surface. Thus, it is quite reasonable to assume that just these AS on the SiO$_2$ surface react first of all with nitroxides. This assumption is supported by the fact that the ESR parameters for nitroxides coordinated by SiO$_2$ are close to those for the same radicals forming hydrogen bonds, involving electron-donating NO groups, with solvent molecules in vitrified solutions [3,4].

Different clusters were used in the scientific literature during the quantum chemical investigations of adsorption on the surface of alumina [13–20]: from very small ones containing only one Al atom [13,14] to very large ones containing hundreds of atoms [15]. At the same time, it was shown [5,6] that even the "minimal" cluster model of surface AS (Al(OH)$_3$) permits the adequate quantum chemical interpretation of the whole set of accumulated radiospectroscopic and thermochemical data on the coordination of nitroxide probes on the surface of alumina to be advanced. In this case, a number of nonempirical and semi-empirical calculations for model cluster PSC were carried out in terms of the unrestricted Hartree–Fock (UHF) approach using the STO-3G, STO-6G, 3-21G, and 6-31G basis sets, or the MNDO, AM1, and PM3 valence approximations [21].

It has been demonstrated [5–8] that the semi-empirical methods are capable of reproducing structural, magnetic resonance, and energy properties of the PSC in question no worse, and in some respects even better, than widely distributed ab initio calculation procedures. Since these methods require much less computation time, they are likely to be preferred for the analysis of complex nitroxide PSC on oxides, studied by the ESR technique [1,2]. Also, it has been found [5] by comparison of various ways of cluster simulation that the best agreement between the calculated and experimental radiospectroscopic and energy quantities of nitroxide PSC on Al$_2$O$_3$ can be achieved when the geometric parameters found for the oxide by crystallographic methods are fixed for the model cluster. Taking the foregoing into account, it would be reasonable to use a similar scheme in cluster quantum chemical calculations of the coordination characteristics of TEMPO (**1**), 2,2,3,4,5,5-hexamethyl-3-imidazolidin-*N*-oxyl

(**2**), 2,2,4,5,5-pentamethyl-3-imidazolin-*N*-oxyl (**3**), 2,4,5,5- tetramethyl- 2- phenyl- 3- imidazolin- *N*- oxyl (**4**), 2,4,5,5-tetramethyl-2-octyl-3-imidazolin-*N*-oxyl (**5**) on the surfaces of alumina, gallia, and partially dehydroxilated silica gel.

Subsequently, the fixed clusters $Al(OH)_3$ and $Ga(OH)_3$ have the shape of a regular truncated tetrahedron in which the length of the intracluster chemical bond Al–O or Ga–O is 1.82 or 1.83 Å (these are the average values found experimentally [22,23]). The covalent clusters simulating the surface acid sites on SiO_2 are constructed from regular silicon–oxygen tetrahedra with an intracluster interatomic distance $r(Si–O)$ equal to 1.62 Å (X-ray diffraction data). Free valences on the boundaries of these clusters are saturated with H atoms. The SiO_4 tetrahedra have fixed structural parameters, but the bond angles between the "coupled" tetrahedra are subjected to variations as the nitroxide radicals are introduced into the system.

In this work, with the aim of testing different computing techniques, the comparative quantum chemical analysis of structure, spin, charge, and energy characteristics of the model coordination of the simplest representative of nitroxides, the $H_2NO^\bullet$ radical, to the oxide cluster AS is firstly carried out. After this, the experimentally studied paramagnetic complexes of TEMPO as well as imidazoline and imidazolidine nitroxides with AS on the surfaces of alumina, gallia, and silica gel are analyzed. The supplementary reason for reference to the prototype $H_2NO^\bullet$ lies in that the previous work [5], concerned with the adsorption of nitroxide probes on the surface of alumina, demonstrated that the implication of $H_2NO^\bullet$ in cluster quantum chemical calculations proved to be sufficient for the consistent semi-quantitative explanation
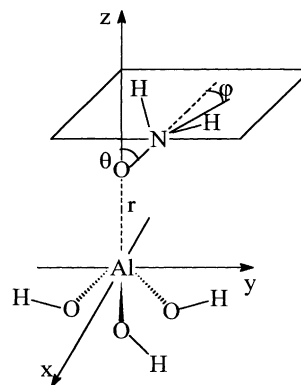
Fig. 2. Nitroxide $H_2NO^\bullet$ coordinated to the model cluster LAS $Al(OH)_3$.

of experimentally established regularities, since the change-over to more complicated, really investigated, nitroxides had no effect on the drawn qualitative conclusions.

3. The nitroxide PSC with the model cluster LAS of alumina

In order to test successively various calculation procedures, it is quite natural to carry out initially comparative quantum chemical analysis of the spatial structure and some properties of the cluster PSC $H_2NO^\bullet \cdots Al(OH)_3$ (see Fig. 2). In Table 1, the proper characteristics calculated by semi-empirical (MNDO, AM1, and PM3) and ab initio (6-31G) methods are compared with those experimentally measured or estimated for typical stable nitroxides. Table 1 lists the lengths of the O–N bond, the θ and φ, angles reflecting the bending and the extent of pyramidality

Table 1
Structural, magnetic resonance, and energy parameters of the cluster PSC $H_2NO^\bullet \cdots Al(OH)_3$

Parameter	MNDO	AM1	PM3	6-31G	Experimental values
$r(O–N)$ (Å)	1.23	1.24	1.26	1.23	1.23–1.30
θ (°)	50	67	71	50	–
φ (°)	25	1	4	25	15–30
a_{iso}^N (G)	27	19	13	42	19–22
ρ^N	0.54	0.61	0.75	0.65	~0.6
ρ^O	0.48	0.43	0.30	0.46	~0.4
$-\Delta E_c$ (kcal mol^{-1})	24.5	21.6	36.3	41.5	30–35

of the $H_2NO^\bullet$ radical, the constants of the isotropic hyperfine coupling (IHFC) with the ^{14}N nucleus, the total spin populations ρ of the N and O atoms, and the energies ΔE_c of the formation of the cluster PSC $H_2NO^\bullet \cdots Al(OH)_3$.

It can be seen from the data of Table 1 that the O–N bond lengths calculated by semi-empirical and nonempirical methods are very similar and close to the reliable reported values ($r(O–N) = 1.2$–$1.3\,\text{Å}$) for most of the nitroxides [24]. The φ angle (between the H–N–H plane and the axis of the O–N bond) differs significantly from zero only within the scope of MNDO and UHF/6-31G approaches, whereas the AM1 and PM3 methods predict this parameter to be very close to zero which is in contrast with the experimental estimates [25] listed in Table 1.

Since the experimental IHFC constants a_{iso}^N for the PSC of nitroxides on the alumina surface are normally 19–$22\,\text{G}$ [1], the values obtained by semi-empirical methods are much more reasonable than that significantly overestimated by the UHF/6-31G procedure. According to all computing schemes, the total spin population of the N atom (ρ^N) in the PSC is somewhat higher than that of the O atom (ρ^O). It is in agreement with the $\rho^N{:}\rho^O$ ratio estimated empirically, i.e. $\sim 0.6{:}0.4$ [25]. It is worth noting that a similar experimental ratio of the total spin populations ρ^N and ρ^O of the N and O atoms in free radicals is inverted ($\rho^N{:}\rho^O \approx 0.4{:}0.6$) [25]. This inversion, which is typical for any nitroxide coordinated through the O atom, seems to be properly reproduced only by the MNDO and AM1 procedures, whereas the UHF/6-31G approach results in the ratio $\sim 0.2{:}0.8$ that is far from to be reasonable. Nevertheless, it is worth noting that in accordance with the experimental data [2], all the above quantum chemical methods predict the growth of the total spin population of the N atom upon coordination.

A valuable characteristic of the coordination is the energy of complex formation (ΔE_c). As is seen from Table 1, the magnitude of this energy obtained by the PM3 method seems to be considerably closer to the experimental data than the rest. It is not surprising, since the PM3 semi-empirical parameterization is above all focused on reproducing the heats of formation of various chemical compounds not infrequently with the detriment to other their properties. The MNDO and AM1 methods underestimate the energy

of complex formation and the UHF/6-31G scheme overestimate this energy. Nevertheless, the values obtained by all the computing methods undoubtedly point to the chemisorption nature of the coordination of nitroxides to the LAS on the Al_2O_3 surface.

Thus, the results presented in Table 1 indicate the semi-empirical approaches to be on the whole not less advantageous than the nonempirical UHF/6-31G method. Taking into consideration this fact and much less computer time required, it is reasonable to analyze the structural, radiospectroscopic, and energy characteristics of the coordination of more complicated nitroxide probes to the surface LAS of alumina within the framework of semi-empirical schemes. Preference is to be given to the MNDO approximation in so far as it has been most widely evaluated [26–30] in quantum chemical calculations of thermodynamic, structural, and magnetic resonance properties of organic and inorganic free radical systems.

Another question to be considered is how the calculated characteristics depend on the size of cluster. To test the stability of the results to the size of cluster and just the use of small clusters, the calculations of $H_2NO^\bullet$ coordinated to the large clusters representing the surface of alumina are performed. To avoid the problems with saturation of the cluster by hydrogen atoms, two uncharged surface clusters $Al_{16}O_{24}$ and $Al_{22}O_{33}$ representing LAS were cut out. The results of the calculations of their complexes with $H_2NO^\bullet$ by MNDO method are presented in Table 2. The comparison of data of Tables 1 and 2 shows that the increase of the cluster size slightly affects on the characteristics of the adsorption of $H_2NO^\bullet$. It is worth noting that the calculations with large clusters predict the values of the IHFC constant a_{iso}^N and the energy

Table 2
Structural, magnetic resonance, and energy parameters of the model PSC of the clusters $Al_{16}O_{24}$ and $Al_{22}O_{33}$ with $H_2NO^\bullet$

Cluster	$Al_{16}O_{24}$	$Al_{22}O_{33}$
$r(O–N)$ (Å)	1.23	1.23
θ (°)	48	47
φ (°)	23	23
a_{iso}^N (G)	25	24
ρ^N	0.53	0.52
ρ^O	0.49	0.49
$-\Delta E_c$ (kcal mol^{-1})	25.8	26.1

of complex formation closer to the experimental ones than the calculations with small clusters. At the same time, all the differences in the calculated properties caused by changes of the cluster size are less than the differences between different calculation schemes (see Table 1). Therefore, the use of small clusters seems to be validated.

3.1. The model PSC of TEMPO and nitroxides of imidazoline and imidazolidine series

When TEMPO (**1**) is adsorbed on alumina surface, two types of LAS are manifested yielding magnetically nonequivalent PSC. It is conventional [1,2,12,31] to identify the first type of LAS as three-coordinated Al^{3+} ions. The magnetic resonance parameters of the resulting PSC depend markedly on the conditions of training of the alumina samples. The constant of IHFC with the ^{14}N nucleus is usually close to 20 G.

As is known [2], owing to specific features of their structures and broad opportunities for varying the substituents, nitroxides **2–5** of the imidazoline and imidazolidine series (Fig. 1) are more sensitive than TEMPO to the characteristic structure of the oxide surface. These radicals are used successfully to study experimentally at the molecular level, the structures of adsorption complexes formed on oxide catalysts and to establish the structures of the surface AS, as well as the orientation and mobility of coordinated paramagnetic species [2]. The experimental constants of IHFC with ^{14}N nucleus in these radicals are smaller ($\sim$15 G) [9] than that for TEMPO ($\sim$20 G).

Special interest in the radiospectroscopic studies of this type of radicals is caused by the fact that they incorporate two (see Fig. 1) electron-donating centers (the N(3) and O atoms) which compete in their coordination to the surface LAS (see Fig. 3). The preferred coordination by one of these centers is largely due to the structure of a particular radical, and can be established experimentally from the ESR spectral pattern and from the magnitude of the IHFC constant of the $^{14}N(1)$ nucleus in the resulting PSC. For example, radical **2** is coordinated exclusively via the O atom, whereas radical **3** is bound via the N(3) atom. In the case of radicals **4** and **5**, a superposition of the ESR spectra is observed, indicating the binding of these radicals with LAS via both the O and N(3) atoms. Nitroxide **1** has only one electron-donating center and is coordinated to LAS merely via the O atom of the paramagnetic N–O group.

Taking into account the experimental data described above, we analyze two structural types of complexes (see Fig. 3) reflecting the opportunities of coordination via both the O and N(3) atoms. The calculated characteristics of the above PSC formed by radicals **1–5** and the model cluster LAS Al(OH)$_3$ are set out in Table 3. It is worth noting that our quantum chemical calculations, like radiospectroscopic studies [1], give evidence of the absence of the coordination through the N(3) atom in the case of imidazolidine nitroxide **2** (no matching stationary point is found on the potential energy surface). Conversely, imidazoline radicals **3–5** (see Fig. 3d) form relatively stable PSC with the cluster LAS Al(OH)$_3$.

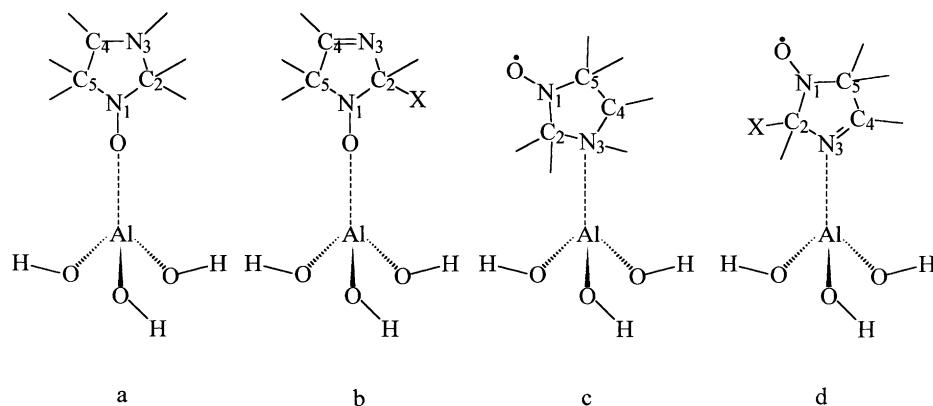

Fig. 3. Imidazolidine and imidazoline nitroxides coordinated via the O and N(3) atoms to the model cluster LAS Al(OH)$_3$.

Table 3
Structural, magnetic resonance, electrostatic, and energy parameters of the cluster PSC formed by radicals **1–5** with the model cluster LAS Al(OH)$_3$[a]

Parameter	1	2	3		4		5	
	O	O	O	N	O	N	O	N
$r(\text{Al}\cdots\text{Y})$ (Å)	1.86	1.86	1.86	1.97	1.86	1.97	1.86	1.98
$r(\text{O–N})$ (Å)	1.23	1.23	1.23	1.22	1.22	1.22	1.23	1.22
φ (°)	17	15	13	17	13	18	15	12
$a_{\text{iso}}^{\text{N}}$ (G)	22	21	22	19	22	19	21	19
ρ^{N}	0.60	0.62	0.61	0.37	0.61	0.39	0.62	0.38
ρ^{O}	0.42	0.40	0.42	0.61	0.44	0.61	0.40	0.61
Q^{Al}	0.95	0.94	0.93	0.87	0.93	0.87	0.93	0.87
$-\Delta E_{\text{c}}$ (kcal mol^{-1})	33.8	29.5	29.4	32.2	29.8	29.2	30.5	29.4

[a] Radicals **1** and **2**: coordination through the O atom; radicals **3–5**: coordination through the O and N atoms; MNDO method.

Comparison of the data listed in Table 3 demonstrates that the length of the donor–acceptor bond Al$\cdots$Y (Y = O, N(3)) depends strongly on the pattern of coordination. As the length of the Al$\cdots$N bond is greater than the length of the Al$\cdots$O bond, then for the coordination via the N(3) atom, the effect of the cluster LAS on the electronic structure and the spin properties of the radical subsystems in the corresponding PSC should be much weaker. For the coordination via the O atom, the O–N bond is somewhat longer than in the case of the coordination via the N(3) atom. It is interesting to note that the MNDO method predicted the angle in all these PSC to be far smaller than that in the H$_2$NO$^\bullet\cdots$Al(OH)$_3$ prototype (cf. Tables 1 and 3).

Owing to the substitution of H$_2$NO$^\bullet$ by real nitroxides **1–5**, the IHFC constant of the ^{14}N(1) nucleus ($a_{\text{iso}}^{\text{N}} \approx 22$ G) in the cluster PSC with the coordination via the O atom is in good agreement with experimental data (see Table 1). The analogous constant in the case of coordination via the N(3) atom is smaller and very close to those peculiar to free nitroxides. This is not surprising inasmuch as the nitroxyl group carrying the unpaired electron is far removed from the site of coordination. For the same reason, the ratio of the total spin populations for these PSC, ($\rho^{\text{N}}:\rho^{\text{O}} \cong 0.4{:}0.6$) is also bound to be characteristic of free nitroxides; this is clearly confirmed by the data of ESR spectroscopy [25]. As could be expected, the positive charge on the Al atom (Q^{Al}) is noticeably smaller when radicals **3–5** are coordinated via the N(3) atom rather than when coordinated via the O atom.

It is of special interest to carry out comparative quantum chemical analysis of the energy characteristics of the coordination of nitroxides **1–5** to the model cluster LAS. As is seen from Table 3, the calculated energies $-\Delta E_{\text{c}}$ of complex formation are all close to 30 kcal mol^{-1}, which is in relatively good agreement with the values found experimentally for the chemisorption of some nitroxides on oxide catalysts [12]. At the same time, the results of these calculations can be used for the estimation of the predominant ways of coordination of radicals **2–5**.

Actually, as was emphasized above, our calculations in conformity with the experimental data [1,2] have shown that imidazolidine radical **2** is prone to coordination only via the O atom. The difference ($\sim$3 kcal mol^{-1}) between the energies of formation of the two types of PSC, found by calculations, serves as a convincing reason for the preferred coordination of radical **3** via the N(3) atom, because according to the Boltzmann distribution, the populations of the above configuration states can differ by more than two orders of magnitude at the standard temperature. The conclusions drawn from the quantum chemical analysis for nitroxides **4** and **5** are not so unambiguous, since the calculated energies of their donor–acceptor binding to the model cluster LAS via the O and N(3) atoms are quite close to each other, apparently due to steric effects that accompany the complex formation. In this case, a superposition of their ESR spectra is to be expected.

4. The nitroxide PSC with the model cluster LAS Ga(OH)$_3$

Gallium is the closest analog of aluminum. Related gallium and aluminum compounds are structurally

similar and have resembling physicochemical properties. Complexes of nitroxide probes with gallium halides and coordinatively unsaturated Ga^{3+} ions on the surface of gallia have been studied in some detail by ESR method [12].

In spite of the similarity of physicochemical properties of related gallium and aluminum coordination compounds, their structural and electronic characteristics can differ appreciably. Changes in geometric and electronic structures of a nitroxide probe caused by the substitution of Al^{3+} by Ga^{3+} in the surface LAS can be readily simulated through the use of cluster versions of quantum chemical computing schemes. For the purpose of evaluating the semi-empirical PM3 approach, we firstly concern ourselves with the model coordination of the simplest nitroxide, $H_2NO^\bullet$, to the cluster LAS $Ga(OH)_3$. The PM3 method is chosen for the reason that it is the only one among modern semi-empirical approximations to have included the parameterization for gallium compounds.

Table 4 lists the results of quantum chemical calculations of the model PSC $H_2NO^\bullet \cdots Ga(OH)_3$, obtained in the UHF approximation using the semi-empirical PM3 approach and ab initio computing scheme in the 6-31G basis set. As can be seen from Table 4 the length of the $Ga \cdots O$ coordination bond $r(Ga \cdots O)$, calculated by the UHF/PM3 method is merely slightly less than that evaluated in the UHF/6-31G approximation. Close $r(O–N)$ distances in the PSC $H_2NO^\bullet \cdots Ga(OH)_3$ are also obtained by both calculation procedures. Despite the difference in the θ angles (see Fig. 2) in the semi-empirical and nonempirical structures of this PSC, their obvious

similarity, i.e. rather strong bending, should be pointed out. Much the same semi-quantitative agreement is observed for the IHFC constant a_{iso}^N and $\rho^N : \rho^O$ ratio (cf. columns 2 and 3 in Table 4).

No experimental data on the chemisorption energies of nitroxides on the surface of gallia are available until recently. As was previously mentioned, the PM3 semi-empirical parameterization was chiefly intended for describing quantitatively the heats of formation of various chemical compounds. Thus, the energies of the complex formation ΔE_c calculated within the scope of this approach seem to be realistic.

To see this, one can compare (Table 4) the $|\Delta E_c|$ value estimated by the PM3 method ($\sim$59 kcal mol^{-1}) with that calculated using the UHF/6-31G scheme ($\sim$62 kcal mol^{-1}). Closeness of these values verifies that the PM3 approach is applicable for obtaining quantitative estimates of the energy characteristics of gallium-containing systems. On the whole, the comparison of all above tabulated data obtained by the UHF/PM3 and UHF/6-31G quantum chemical computing procedures demonstrates their equivalence in reproducing the numerical values of physicochemical quantities that have not been determined experimentally.

4.1. The model PSC of TEMPO (1)

The results of calculations of the PSC TEMPO$^\bullet \cdots$ $Ga(OH)_3$ are listed in Table 4 (column 4). Most of the qualitative regularities evaluated for the simplest nitroxide PSC, $H_2NO^\bullet \cdots Ga(OH)_3$, seems to be also valid in this case. At the same time, certain differences manifest themselves.

As is readily seen from comparison of the ΔE_c values in Tables 1, 3 and 4, the PSC TEMPO$^\bullet \cdots Ga(OH)_3$ and $H_2NO^\bullet \cdots Ga(OH)_3$ are much more stable than their analogs TEMPO$^\bullet \cdots Al(OH)_3$ and $H_2NO^\bullet \cdots Al(OH)_3$. With the exception of the energy of complex formation (ΔE_c), the Ga–O coordination bond length and other structural and magnetic resonance parameters of the nitroxide PSC with the model LAS $Ga(OH)_3$ are almost insensitive to the substitution of TEMPO by $H_2NO^\bullet$. It is important to note that the PSC TEMPO$^\bullet \cdots Ga(OH)_3$ is bent stronger than its analog TEMPO$^\bullet \cdots Al(OH)_3$. The high energy of complex formation ($\sim$75 kcal mol^{-1})

Table 4
Structural, magnetic resonance, and energy parameters of the cluster PSC formed by $H_2NO^\bullet$ and TEMPO radicals with the model cluster LAS $Ga(OH)_3$

Parameter	$H_2NO^\bullet \cdots Ga(OH)_3$		TEMPO$^\bullet \cdots Ga(OH)_3$
	PM3	6-31G	PM3
$r(Ga \cdots O)$ (Å)	1.82	1.85	1.81
$r(O–N)$ (Å)	1.26	1.25	1.27
θ (°)	72	52	69
a_{iso}^N (G)	12	18	13
ρ^N	0.77	0.64	0.71
ρ^O	0.26	0.45	0.25
$-\Delta E_c$ (kcal mol^{-1})	59.2	62.3	76.4

gives an unambiguous evidence for the chemisorption character of the donor–acceptor interaction between the TEMPO radical and the Ga(OH)$_3$ cluster LAS.

Usually, a particular interest is given to comparing the acidity of various surface LAS. With this aim in view, one may take advantage of both the charge Q^M on the metal atom and the energy ε_v of the lowest unoccupied molecular orbital (LUMO) of a model cluster as a quantum chemical index of acidity. These quantities calculated within the scope of the PM3 scheme for the Ga(OH)$_3$ and Al(OH)$_3$ model cluster LAS are indicative of the gallium-containing LAS to be more acid than the aluminum-containing analog, as far as $Q^{Ga} > Q^{Al}$ and $\varepsilon_v^{Ga} < \varepsilon_v^{Al}$ (1.22 versus 0.89 and -2.5 versus -1.6 eV, respectively).

It is worth noting that all the above conclusions drawn from the quantum chemical analysis performed are in agreement with the previous deductions based on the generally accepted interpretation of experimental data including radiospectroscopic results [12]. There is no doubt that consideration of more complicated cluster models of the LAS structures on the oxide surface could exert some influence on the characteristics of their coordination binding with nitroxide probes, as found by semi-quantitative calculations. However, it should be emphasized that using a relatively simple model of the cluster LAS, we succeeded in elucidating the experimentally revealed regularities of the coordination of nitroxide probes to the surface LAS of gallia and alumina as well as in argumentative estimation of the heat of such a chemisorption process, remaining so far undetermined experimentally in the case of gallia.

5. The nitroxide PSC on the silica surface

The whole set of experimental data [3,4] indicates that the surface of silica gel, even when it is dehydroxylated under severe conditions, contains closely located "paired" silanol groups. It has been assumed [32] that geminal OH groups can act as the adsorption AS. In this section, we shall concern ourselves with a simple cluster model of this type of OH groups as well as with more complicated cluster structures.

5.1. The model PSC of imidazoline nitroxides

ESR spectra provide valuable information about the mechanism of coordination of nitroxides of the imidazoline series to the surface AS of silica with various degrees of dehydroxylation [3,4]. In particular, the rotational mobility of radicals **3** and **4** (containing two electron-donating sites), measured experimentally under similar conditions on silica [3], is substantially lower than that of radical **1** containing only one electron-donating group. Based on these experimental data, it was concluded [3] that two-center adsorption of imidazoline radicals on silica was observed. This conclusion has been confirmed by the results of electron spin echo studies [33] of the orientational motion of nitroxides coordinated to a surface.

When the temperature rises, the rotational mobility of radicals **3** and **4** increases, and the shapes of the transformed ESR spectra as well as correlation times τ_c point to the fact that the two-center coordination on the surface AS of silica gel is converted into one-center coordination. This process is reversible. The standard enthalpies of the transition ($\Delta H^0 \approx$ 7–9 kcal mol^{-1}) are fairly close to the heats of formation of hydrogen bonds between the silica AS and typical electron-donating molecules, while the entropy increments ΔS^0 are ~20 cal mol^{-1} K^{-1}, giving evidence for a pronounced change in the number of degrees of freedom in the course of the coordination transformation [3].

Based on the analysis of the ESR spectral patterns and the magnitudes of anisotropic hyperfine coupling (AHFC) constants in imidazoline radicals, it was concluded [3] that the hydrogen bonds between the O atoms of the radical ON groups and the H atoms of the silica surface AS cleave when the temperature rises. It is worth noting that the presence of a large volume substituent in the imidazoline ring (radicals **3** and **4**) has virtually no effect on the characteristics of coordination.

To interpret the ESR spectra of imidazoline PSC on the silica surface, we analyzed the one-center (via the O or N(3) atom) coordination to the model cluster AS Si(OH)$_4$ (see Fig. 4), and the imagined PSC formed upon binding of both electron-donating atoms (O and N(3)) to a "pair" of AS represented by geminal (Fig. 4), vicinal, and "tetrahedron-separated" silanol groups (see Fig. 5). The results of MNDO calculations
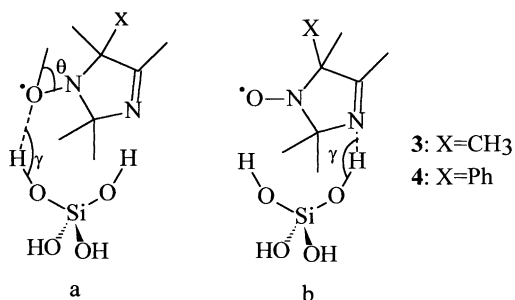
Fig. 4. Imidazoline nitroxides coordinated via the O and N(3) atoms to the model cluster AS Si(OH)$_4$.

Table 5
Structural, magnetic resonance, and energy parameters of the cluster PSC formed by radicals **3** and **4** with the model cluster AS Si(OH)$_4$[a]

Parameter	**3**		**4**	
	O	N	O	N
$r(H \cdots Y)$ (Å)	1.79	1.92	1.83	1.95
$r(O–N)$ (Å)	1.22	1.22	1.22	1.22
θ (°)	19	–	22	–
φ (°)	11	16	12	16
a_{iso}^{N} (G)	22	19	22	20
ρ^{N}		0.57	0.41	0.56	0.41
ρ^{O}		0.44	0.58	0.46	0.59
$-\Delta E_c$ (kcal mol^{-1})	9.1	16.1	8.9	15.9

[a] Coordination through the O and N atoms; MNDO method.

of the characteristics of one-center coordination for radicals **3** and **4** are summarized in Table 5. It can be readily seen from Table 5 that the representative geometric parameters of nitroxides such as the O–N bond length and the φ angle (between the C(2)–N(3)–C(5) plane and the N(1)–O axis; cf. Fig. 1) do not depend significantly on the coordination type, even though the hydrogen bond H$\cdots$N is considerably longer than the H$\cdots$O bond.

Our calculations, in agreement with the experimental results [3,4], lead to the increased IHFR constants a_{iso}^{N} for the cluster PSC in which radicals **3** and **4** are coordinated through the O atom. The calculations reproduce qualitatively correct the increase in the spin population ρ^{N} on the N atom, detected experimentally upon this type of coordination. As is seen from Table 5, this increase is so strong that it results in an inverted $\rho^{N}:\rho^{O}$ ratio in contrast with the ratio obtained for one-center coordination via the N(3) atom. In the second instance, all the structural and magnetic resonance characteristics of the NO group in the PSC

are practically identical to those for free radicals **3** and **4**. It is due to the relative insensitivity of the NO group to the coordination by the remote N(3) atom.

It is worth noting that the hydrogen bonds for both types of the PSC are linear ($\gamma = 180°$). The calculated energies of complex formation ΔE_c point to the considerably higher (by ∼7 kcal mol^{-1}) stability of one-center adsorption forms in which imidazoline radicals are coordinated via their second electron-donating position rather than via the NO group. This is also unambiguously indicated by the temperature dependencies [3] of line shapes in the corresponding ESR spectra and of AHFC constants.

In a quantum chemical analysis of the experimentally studied [3,4] two-center coordination of radicals **3** and **4** on the surface of partially dehydroxylated silica gel, we have used the above-mentioned three model cluster structures containing geminal, vicinal, and "tetrahedron-separated" OH groups. The starting
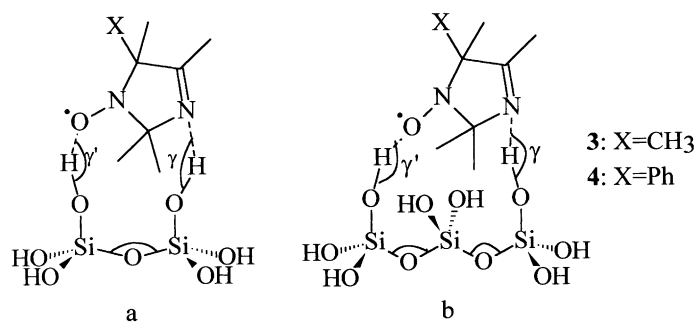

Fig. 5. Two-center coordination of imidazoline nitroxides to the model cluster AS Si$_3$O$_{10}$H$_8$.

geometry to be subjected to the optimization specified above for each PSC studied corresponded to the presence of two typical hydrogen bonds N–O$\cdots$H–O–Si and N$\cdots$H–O–Si with lengths of $\sim$1.8 and 1.9 Å, respectively.

As our MNDO calculations show, such two-center coordination of imidazoline radicals **3** and **4** to the geminal silanol groups is energy unfavored, which can be explained exclusively by geometric reasons. Analogous calculations performed by us in the case of vicinal silanol groups (see Fig. 5a) also rule out the possibility of two-center coordination of imidazoline radicals, since their assumed two-point adsorption forms convert in the course of full geometry optimization into a single-point one ($\gamma = 180°$) with bonding via the N(3) atom. Moreover, when the lengths of both hydrogen bonds in these PSC were not varied and their magnitudes were taken as equal to those given in Table 5, such "forced" two-center coordination of nitroxides **3** and **4** at the vicinal silanol groups was energy unfavorable by more than 10 kcal mol^{-1} because of artificially induced structural strains arising due to the requirement of partial optimization of radical geometry.

Further insertion of one silicon and oxygen tetrahedron between the vicinal silanol groups substantially increases the distance between these surface AS. The calculated parameters of PSC formed by radicals **3** and **4** with such model cluster AS (see Fig. 5b) are listed in Table 6. It is easy to see that both hydrogen

bonds, H$\cdots$O and H$\cdots$N(3), in the two-center PSC (Table 6) are somewhat longer than those in the corresponding one-center PSC (Table 5) and are slightly nonlinear (γ and γ' differ from 180°). This finding shows that there are small structural strains in such an adsorption form.

From comparison of Tables 5 and 6, it is obvious that the IHFC constants a_{iso}^N and the spin populations ρ^N and ρ^O of the N(1) and O atoms in the two-center PSC are much the same as those in the one-center PSC with binding via the O atom (Table 5). The differences in the ΔE_c values are an indication of the preference of the simultaneous coordination of radicals **3** and **4** by both their electron-donating sites rather than via a single N(3) atom. This difference is $\sim$8 kcal mol^{-1} and is in good agreement with the experimental data [3]. The insensitivity of the calculated radiospectroscopic and energy characteristics of PSC to the presence of a fairly voluminous phenyl group in the imidazoline ring also has experimental confirmation [3].

It is worth noting that the results obtained upon extension of the cluster model $Si_3O_{10}H_8$ by adding one more silicon and oxygen tetrahedron followed by analogous calculations with partial geometry optimization (viz. the Si–O–Si angles between the "coupled" tetrahedra; see above) were practically identical to the results presented in Table 6.

6. Conclusions

Stable nitroxides frequently prove to be practically convenient and highly informative probes in inquiring into the nature of the surface AS on the oxide catalysts and carriers. Thanks to the extremely high sensitivity of the spin-Hamiltonian parameters to various coordination factors, the ESR spectra of coordinated nitroxides can be used successfully to solve structural–chemical problems concerned with the reliable identification of the donor–acceptor PSC, which is needed for advancing the deep insight into the elementary stages of acid–base processes with the participation of reactive AS. However, reliable interpretation of radiospectroscopic information about structural and other physicochemical properties of the resulting PSC usually involves the performance of rather complicated quantum chemical calculations of

Table 6

Structural, magnetic resonance, and energy parameters of the cluster PSC formed by radicals **3** and **4** with two AS of the model cluster $Si_3O_{10}H_8$[a]

Parameter	**3**	**4**
$r(\text{H}\cdots\text{O})$ (Å)	1.82	1.86
$r(\text{H}\cdots\text{N})$ (Å)	1.93	1.96
$r(\text{O–N})$ (Å)	1.22	1.22
θ (°)	58	60
γ (°)	179	178
γ' (°)	176	178
φ (°)	12	14
a_{iso}^N (G)	22	22
ρ^N	0.54	0.55
ρ^O	0.46	0.44
$-\Delta E_c$ (kcal mol^{-1})	24.3	23.7

[a] MNDO method.

magnetic resonance parameters by adequate ab initio or semi-empirical methods.

The results of the cluster quantum chemical calculations of structural, magnetic resonance, and energy quantities indicate that semi-empirical approaches of the MNDO type can reproduce the whole set of these properties characterizing the coordination of nitroxides even more adequately than widely distributed ab initio methods. Within the scope of the cluster approach under examination, some exceptional features of the ESR spectra of imidazolidine and imidazoline nitroxides coordinated to alumina surface can be convincingly interpreted. A noncontradictory treatment of these features resolves itself into that through the energy effects, for example radical **2** is coordinated to the surface LAS exclusively via its O atom and radical **3** is bound predominantly via the N atom, whereas in the case of radicals **4** and **5**, the ESR spectrum represents the competition between the two electron-donating centers for coordination to the LAS.

It is important to note that the results of our quantum chemical calculations indicate the majority of general qualitative regularities to be successfully elucidated even using a relatively simple cluster model for the surface LAS. Furthermore, such a model has made it possible to draw the conclusion that the LAS on the surface of gallia are more acid than those on the alumina surface. Complex formation of the paramagnetic nitroxide probes with the diamagnetic surface LAS containing three-coordinated gallium or aluminum ions is a chemisorption process, the donor–acceptor complexes formed on Ga_2O_3 being much more stable than their analogs on Al_2O_3.

The results of quantum chemical analysis performed reveal that nitroxides of the imidazoline series are capable to form both one-center and two-center PSC with the different AS of partially dehydroxylated silica gel. To judge by the calculated complex formation energies ΔE_c, these radicals explicitly prefer in the case of single-point adsorption to be coordinated to such AS via the N(3) atom of the five-membered ring rather than via the nitroxyl group, whereas for similar imidazoline PSC formed with the surface LAS on Al_2O_3, the difference in energies of complex formation ΔE_c is not so pronounced. Lastly, we would like to stress that the "optimal" $Si_3O_{10}H_8$ cluster allows an adequate quantum chemical interpretation of the whole range of accumulated radiospectroscopic

and thermochemical data on the adsorption of paramagnetic imidazoline derivatives on the surface of silica to be proposed. Simpler cluster constructions containing only vicinal or, especially, geminal silanol groups are unsuitable for this purpose, because the two-center coordination of imidazoline radicals to the groups indicated proves to be energy inconsistent due to pronounced structural strains.

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