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Quantum-chemical analysis of the coordination of nitroxide probes by Lewis acid sites on the surface of Al_2O_3

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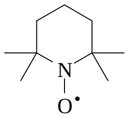
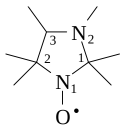
The results of radiospectroscopic investigations of complexes of nitroxides with Lewis acid sites on an alumina surface are interpreted using quantum-chemical analysis.

The method of paramagnetic complexes of probe molecules is used successfully to study acidic properties of oxide catalysts and the structures of surface proton and Lewis acid sites (LAS). Stable nitroxides are used most frequently as convenient probes providing a lot of information. When these species are adsorbed on oxides possessing proton and Lewis acidity, donor–accept or surface complexes (SC) are formed; these complexes, like the initial nitroxides themselves, can be studied by EPR spectroscopy.[1–6]

The information content of EPR spectra can be markedly increased by quantum-chemical analysis of the radiospectroscopic and energy characteristics of the complexes formed. Therefore, we attempted to analyse the structures and properties of a number of nitroxide complexes that have been studied experimentally,[2–5] namely, the complexes of 2,2,6,6-tetramethylpiperidin-*N*-oxyl (TEMPO), 2,2,3,4,5,5-hexamethyl-3-imidazolidin-*N*-oxyl **1**, 2,2,4,5,5-pentamethyl-3-imidazolin-*N*-oxyl **2**, 2,4,5,5-tetramethyl-2-phenyl-3-imidazolin-*N*-oxyl **3** and 2,4,5,5-tetramethyl-2-octyl-3-imidazolin-*N*-oxyl **4** with the surface LAS of alumina.



TEMPO



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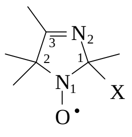

2 X = Me
3 X = Ph
4 X = C_8H_{17}

Since it has been shown experimentally that the magnetic resonance parameters of donor–acceptor complexes of nitroxides with $AlCl_3$ in non-polar solvents are similar to those of their complexes with the surface LAS of alumina,[2] the latter were modelled by the covalent cluster $Al(OH)_3$. This approach has been widely tested in non-empirical and semi-empirical quantum-chemical calculations of chemisorbed molecular forms.[7]

In this work, all quantum-chemical calculations were performed by unrestricted Hartree–Fock (UHF) methods; non-empirical calculations were carried out in the STO-3G, STO-6G, 3-21G and 6-31G basis sets, while semi-empirical calculations were accomplished within the framework of MNDO, AM1 and PM3 approximations. In order to compare the efficiencies of these methods, we studied initially the simplest nitroxide H_2NO (Table 1) and its complex $H_2NO\cdots Al(OH)_3$ (Figure 1, Table 2). Comparison of the values presented in Tables 1 and 2 shows that generally, the MNDO method provides better agreement with the N–O bond lengths, spin populations (ρ) of the N and O atoms and isotropic hyperfine coupling constants with the ^{14}N nucleus found experimentally for nitroxides than any other method mentioned above; in addition, this method is much more economical than other methods, especially, than the non-empirical UHF/6-31G variant. Therefore, it is the MNDO method that has been used subsequently for quantum-chemical analysis of coordination of the more complicated probe nitroxides listed above.

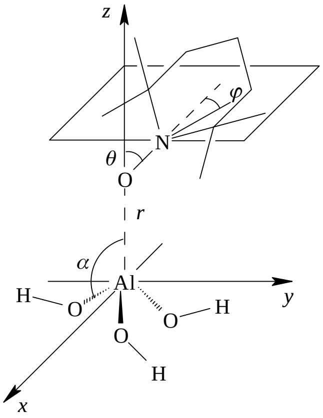

Figure 1 Cluster paramagnetic SC of the simplest nitroxide with the model LAS on Al_2O_3.

When TEMPO (Figure 2) is adsorbed on an alumina surface, two types of LAS giving magnetically non-equivalent SC can be observed. LAS of the first type are usually identified[2–5] as tricoordinated Al^{3+} ions. The way of modelling these SC is of primary importance for the calculations of structures of this sort.

The TEMPO radical and the two forms of its paramagnetic SC with the cluster LAS are considered below. The first structural type of SC (I) being modelled corresponds to full optimization of the geometry of both the nitroxide and the $Al(OH)_3$ cluster. If we assume that the aluminum–oxygen fragment in alumina is a fairly rigid ('frozen') structure, we pass to structural type II. In this case, optimisation is carried out only for the geometry of the coordinated radical, whereas

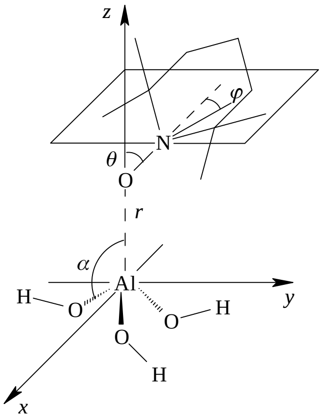

Figure 2 Cluster paramagnetic SC of TEMPO with the model LAS on Al_2O_3.

Table 1 Structural and magnetic-resonance characteristics of the H_2NO radical.

Method	r(O–N) /Å	a_{iso}^{N}/G	ρ^{N}	ρ^{O}
MNDO	1.22	13	0.45	0.60
AM1	1.22	15	0.51	0.54
PM3	1.23	10	0.64	0.40
STO-3G	1.34	3	0.10	0.93
STO-6G	1.34	3	0.10	0.93
3-21G	1.34	10	0.18	0.87
6-31G	1.30	17	0.24	0.81
Exp[a]	1.23–1.25	15–19	~0.4	~0.6

[a] Experimental data (last row) correspond to typical stable nitroxides.[1,6,10] It should be mentioned that for H_2NO itself there are no experimental data on the N–O bond length, though the isotropic hyperfine coupling constant for the ^{14}N nucleus has been recorded: a_{iso}^{N} 12 G.

Table 3 Characteristics of the SC of TEMPO with the model cluster LAS found by MNDO calculations.[a]

Complex type	r(Al···O)/Å	φ	a_{iso}^{N}/G	ρ^{N}	ρ^{O}	E_c/ kcal mol^{-1}
TEMPO	–	19°	20	0.40	0.59	–
SC I	1.98	18°	22	0.61	0.41	–18.7
SC II	1.86	17°	22	0.60	0.42	–33.8

[a] SC I in which all geometric parameters have been allowed to relax is 11.9 kcal mol^{-1} more stable than SC II.

the fixed cluster has the shape of a regular truncated tetrahedron in which the length of the intracluster Al–O chemical bond is 1.82 Å (it is the average value for -Al_2O_3 determined experimentally[8] from the shift of the fluorescence lines of AlK).

The results of the calculations (Table 3) indicate that the geometry of the paramagnetic SC is sensitive to the type of cluster model used. The maximum variations are observed in the length of the Al···O donor–acceptor bond. At the same time, as has been shown in a previous study,[9] the role of the proximity of the N atom to the pyramidal shape (the φ angle) can be neglected as the first approximation in the modelling of the coordination.

Both structural types of the model paramagnetic SC are characterised by an inversed ratio of the total spin populations (ρ^{O}:ρ^{N} 0.4:0.6) with respect to that typical of free TEMPO radicals (ρ^{O}:ρ^{N} 0.6:0.4). An increase in the spin density of the nitrogen atom following coordination of TEMPO to the surface LAS is in agreement with experimental data.[2–5]

The energy of complex formation (E_c) makes it possible to distinguish between the two structural types of the model SC of TEMPO, because, on the one hand, it has been measured experimentally and, on the other hand, it is fairly sensitive to the structure of the cluster LAS. Despite the fact that in both cases this quantity attests to the fact that TEMPO interacts with the LAS on Al_2O_3 by a purely chemisorption mechanism (Table 3), only in the case of SC II containing a 'frozen' cluster is its magnitude in good agreement with the experimental results (32–35 kcal mol^{-1}).

It is known that,[3] owing to specific features of their structures and the broad opportunities for varying the substituents, nitroxides **1**–**4** of the imidazoline and imidazolidine series are more sensitive to the structure of the oxide surface than TEMPO. Using these radicals, the structures of the adsorption complexes formed on oxide catalysts and the structures of the surface active sites have been studied successfully experimentally at the molecular level, and the orientation and mobility of coordinated paramagnetic species have been established.[3,10]

Special interest in the radiospectroscopic studies of this type of radicals is caused by the fact that they incorporate two electron donating centres (the N atom and the N–O group), which compete in their coordination to the surface LAS. The preferred coordination to one of these centres is largely due to the structure of a particular radical and can be established experimentally from the EPR spectral pattern and from the magnitude of the hyperfine coupling constants of the ^{14}N nucleus in the SC formed. Thus the radical **1** is coordinated exclusively through the O atom, whereas the radical **2** is bound *via* the N atom. In the case of the radicals **3** and **4**, a superposition of the EPR spectra is observed indicating their binding with LAS *via* both the N and O atoms.[3]

Table 2 Structural and magnetic-resonance characteristics of the $H_2NO\cdots Al(OH)_3$ cluster paramagnetic SC.

Method	r(O–N) /Å	φ	a_{iso}^{Al}/G	a_{iso}^{N}/G	ρ^{N}	ρ^{O}
MNDO	1.23	28°	–2	28	0.48	0.52
AM1	1.24	20°	–2	25	0.61	0.43
PM3	1.27	0°	–2	13	0.75	0.30
STO-3G	1.39	57°	–7	3	0.02	0.98
STO-6G	1.37	66°	–8	4	0.04	0.96
3-21G	1.31	12°	–7	27	0.46	0.64
6-31G	1.27	3°	–8	34	0.51	0.59
Exp[a]	1.23–1.25	15°–30°	~–11	19–22	~0.6	~0.4

[a] Experimental data (last row) correspond to the majority of nitroxides studied.[2–5]

In view of the results of the analysis for TEMPO, it would be of interest to compare the energies of various types of coordination of the radicals **1**–**4**. As in the case of TEMPO, adsorption energies close to those found experimentally have been obtained in the calculations with a fixed cluster geometry. Therefore, in elucidating the preferred method of coordination of the radicals **1**–**4**, it is reasonable to consider the data of these calculations (Table 4).

Our calculations have shown, in conformity with the experimental data,[3,4] that the imidazolidine radicals are prone to coordinate by the O atom. The difference, equal to ~3 kcal mol^{-1}, between the energies of formation of the two types of paramagnetic SC found by calculations is strong evidence for the preferred coordination of the radical **2** through the N atom, because, according to the Boltzman distribution, the populations of the above configuration states may differ by more than two orders of magnitude at the standard temperature. The conclusions drawn from the quantum-chemical analysis for the nitroxides **3** and **4** are not so unambiguous, since the calculated energies of their donor–acceptor binding to the model cluster LAS *via* the nitrogen and oxygen atoms are very close to each other, apparently, due to steric effects that accompany the complex formation.

All the structural conclusions from the cluster quantum–chemical analysis performed are in agreement with the previous conclusions based on the generally accepted interpretation of experimental data including radiospectroscopic results.[4] There is no doubt that consideration of more complicated cluster models of the surface active sites of alumina could exert a substantial influence on the characteristics of their coordination binding with nitroxide probes found by semi-quantitative calculations. However, the results of our quantum-chemical calculations (Tables 1–4) indicate that general qualitative regularities can be successfully elucidated even using a relatively simple model of the cluster LAS.

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Table 4 Energies of coordination (E_c/kcal mol^{-1}) of the radicals **1**–**4** with model cluster LAS found by MNDO calculations.

Radical	Coordination *via* N	Coordination *via* O
1	–	–29.5
2	–32.2	–29.4
3	–29.2	–29.8
4	–29.4	–30.5

References

1 A. L. Buchachenko and A. M. Vasserman, *Stabil'nye radikaly* (*Stable radicals*), Mir, Moscow, 1973, p. 408 (in Russian).

2 V. B. Golubev, E. V. Lunina and A. K. Selivanovsky, *Usp. Khim.*, 1981, **50**, 792 (*Russ. Chem. Rev.*, 1981, **50,** 421).

3 E. V. Lunina, G. L. Markaryan, O. O. Parenago and A. V. Fionov, *Colloids and Surfaces*, 1993, **72**, 333.

4 E. V. Lunina, in *Kataliz* (*Catalysis*), eds. O. A Petrii and V. V. Lunin, MGU, Moscow, 1987, p. 287 (in Russian).

5 E. V. Lunina, *Appl. Spectroscopy*, 1996, **50**, 1413.

6 E. G. Rosantsev and V. D. Sholle, *Organicheskaya khimiya svobodnykh radikalov* (*Organic Chemistry of Free Radicals*), Khimiya, Moscow, 1977, p. 344 (in Russian).

7 N. D. Chuvylkin, *Zh. Fiz. Khim.*, 1985, **59**, 1085 (*J. Phys. Chem. USSR*, 1985, **59**, 634).

8 A. J. Leonard, P. N. Semaille and J. J. Fripiat, *Proc. Brit. Ceram. Soc.*, 1969, 103.

9 A. V. Fionov, E. V. Lunina and N. D. Chuvylkin, *Zh. Fiz. Khim.*, 1993, **67**, 485 (*Russ. J. Phys. Chem.*, 1993, **67**, 436).

10 L. B. Volodarskii, I. A. Grigor'ev, S. A. Dikanov, V. A. Reznikov and G. I. Schukin, *Imidazolinovye nitroksil'nye radikaly* (*Imidazolin nitroxides*), Nauka Sib. Otd., Novosibirsk, 1988, p. 216 (in Russian).

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