Cluster models in the quantum-chemical analysis of the coordination of imidazoline nitroxides on the surface of silica gel

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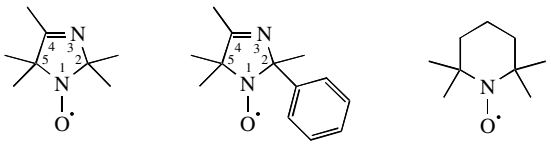
A 'minimal' cluster quantum-chemical model of paired acid sites on the surface of SiO_2 is presented; the model provides adequate explanation of the radiospectroscopic and thermochemical data available on the two-centre and one-centre adsorption of nitroxide probes on the silica surface.

The method of paramagnetic surface complexes (PSC) of probe molecules with active solid state centres has been used successfully to study the structures and properties of oxide surfaces. EPR spectroscopy enables a number of physico-chemical characteristics of the PSC formed to be determined reliably, and coordination phenomena which are observed on oxides[1–3] to be better understood, based on the data obtained by making use of adequate quantum chemical methods.

During the past few years interest in the use of stable imidazoline and imidazolidine nitroxides such as 2,2,4,5,5-pentamethyl-3-imidazolin-*N*-oxyl **1** and 2-phenyl-2,4,5,5-tetramethyl-3-imidazolin-*N*-oxyl **2** as the paramagnetic probes has increased markedly. This is due to such 'bifunctional' radicals possessing two alternate electron-donating centres that usually compete in PSC formation. This is why the structural-chemical information content of EPR spectra is so extensive.[4–6]

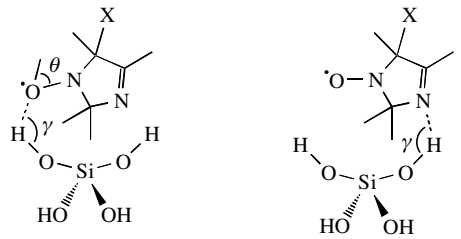


1 **2** **3**

The opportunity for the simultaneous coordination of a 'bifunctional' nitroxide radical at both its electron-donating centres allows the relative arrangement of surface acid sites on oxides to be studied at the molecular level. In particular, EPR spectroscopy has been applied to investigations of the coordination of imidazoline and imidazolidine nitroxides on the silica surface with differing degrees of dehydroxylation. In this case the recorded characteristics of the EPR spectra were qualitatively interpreted by making use of an assumption suggesting that the two electron-donating centres in the nitroxide radical were involved in donor-acceptor binding with the paired neighbouring acid sites of silica gel.[5,6]

It is widely known that silanol groups are typical adsorption centres on the silica surface. Thus, it is quite natural to assume that imidazoline radicals chiefly interact with just such acid sites on SiO_2. Under similar conditions the experimentally measured[5] rotational mobility of these radicals on silica gel was substantially less than that of the TEMPO radical **3** containing merely a single electron-donating group. Based on these experimental data it was concluded that two-centre adsorption of imidazoline radicals on silica was achieved. This conclusion has been confirmed by the results of studies on the orientation motion of coordinated nitroxides by an electron spin echo method.[7]

When the temperature rises the rotational mobility of imidazoline radicals increases, and the shapes of the transformed EPR spectra, as well as the correlation times τ_c, point to the fact that the hydrogen bonds between the oxygen atoms of the radical NO groups and the hydrogen atoms of the silica surface acid sites are broken. This phenomenon is reversible and there

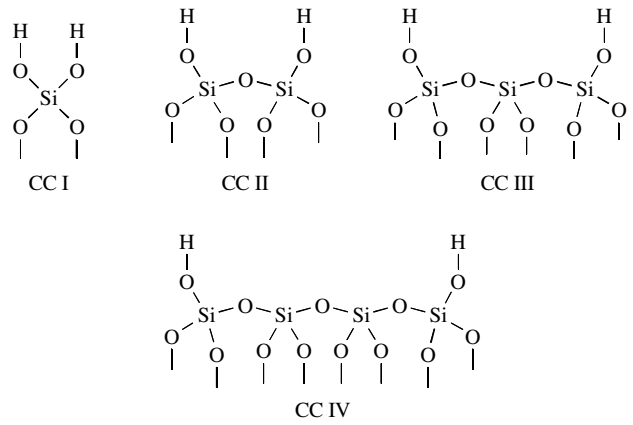


1 X = Me
2 X = Ph

Figure 1 Cluster one-centre PSC of imidazoline nitroxides with model acid site $Si(OH)_4$.

is consequently a dynamic equilibrium between fast- and slow-rotating adsorption forms of imidazoline radicals. Temperature dependences of the proportions of these adsorption forms allow the thermodynamic characteristics of the process to be established. In particular, the standard enthalpies of the transition ($H^0 \sim 7$–9 kcal mol^{-1}) are sufficiently close to the heats of formation of the hydrogen bonds between the silica acid sites and the typical donor molecules, while the entropy increments S^0 are *ca.* 20 cal mol^{-1} K^{-1} , providing evidence for a pronounced change in the number of degrees of freedom in the course of the coordination transformation.[5]

In view of the insufficient completeness and certain ambiguity or 'indirectness' of the structural–chemical information obtained in the above-mentioned radiospectroscopic investigations, we attempted quite naturally to verify the adequacy of the concepts established in so doing with the help of quantum-chemical calculations using the PSC model. This work is devoted to the quantum-chemical analysis of EPR data on the coordination of imidazoline nitroxides such as 2,2,4,5,5-pentamethyl-3-imidazolin-*N*-oxyl **1** and 2-phenyl-2,4,5,5-tetramethyl-3-imidazolin-*N*-oxyl **2** on the surface acid sites of the partially dehydroxilated silica gel.



CC I CC II CC III

CC IV

Table 1 Structural, magnetic resonance, electrostatic and energy characteristics of free imidazoline radicals and their PSC with the $Si(OH)_4$ model cluster acid sites.

Bond type	Radical	r(H···X)/Å	θ/°	γ/°	φ/°	a^N_{iso}/G	$\rho^{N(1)}$	ρ^O	Q^R	|μ|/D	E_c/ kcal mol^{-1}
—	**1**	—	—	—	1 7	19	0.40	0.59	0.00	2.5	—
	2	—	—	—	1 8	20	0.41	0.59	0.00	2.4	—
H···O	**1**	1.79	19	180	11	22	0.57	0.44	0.25	5.6	–9 .1
	2	1.83	22	180	12	22	0.56	0.46	0.25	5.4	–8 .9
H···N(β)	**1**	1.92	—	180	16	19	0.41	0.58	0.25	3.7	–16.1
	2	1.95	—	180	16	20	0.41	0.59	0.26	3.7	–15.9

As in the preceding work[3,8] the calculations of structural, magnetic resonance, electrostatic and energy quantities were performed by a semi-empirical MNDO method and there was demonstrated that this method was capable of representing these properties of the model cluster PSC no worse, and in some respects even better, than widely-distributed *ab initio* calculation procedures. As was shown,[3,8] the best agreement between the calculated and experimental radiospectroscopic and energy quantities can be achieved with a fixed geometry of the model cluster with the structural parameters determined for the oxide by crystallographic methods. Thus in the present work the structurally rigid geometric parameters were assumed to be 'frozen' (c ompletely unchanging).

The covalent clusters as models for the surface acid sites on SiO_2 were constructed from regular truncated tetrahedrons with an intracluster interatomic distance r(Si–O) equal to 1.62 Å Free valencies on the boundaries of these clusters were saturated with hydrogen atoms. The structural parameters of the coordinated imidazoline nitroxides and OH groups directly in contact with them, as well as the Si–O–S i angles between the 'coupled' silicon-oxygen tetrahedrons, were subjected to variations. It means that the SiO_4 tetrahedra had fixed geometries but the bond angle between the tetrahedra was altered as the nitroxide radicals were introduced into the system. The Hartree–Fock value of the proportionality coefficient between the spin density ρ^N_s of the valence s-atomic orbital and the isotropic hyperfine coupling constant a^N_{iso} was used for the nitrogen atom nucleus.

The results of the calculations on free radicals **1** and **2** as well as their complexes (Figure 1) with coordination *via* the O or N(3) atom are summarized in Table 1. It is seen from the analysis of these data that all kinds of coordination features are insensitive to the presence of a large volume substituent at position 2 of the imidazoline ring. Under both methods of coordination linear hydrogen bonds appear, while the radical as a whole is nonlinearly coordinated. The hydrogen bond N···H–O–S i is somewhat longer than the O···H–O –S i bond. Coordination *via* the O atom inverts (in a way peculiar to free nitroxides) the ratio of spin densities ρ^O:$\rho^{N(1)}$ of the O and N(1) atoms, and such an inversion has been observed experimentally. In contrast, with adsorption *via* the N(3) atom all structural and magnetic resonance parameters of the NO group in the PSC formed are practically identical to those peculiar to the free radicals **1** and **2**. This is due to the relative insensitivity of the NO group to coordination *via* the distant N atom.

According to the data in Table 1 the positive charge Q^R acquired by the imidazoline nitroxide is independent of the electron-donating site [O or N(3)] involved in coordination with the model cluster acid site, *i.e.* $Si(OH)_4$. However, the electric dipole moments |μ| of differing PSC are distinguished in these cases by almost 2 D. The calculated complexation energies E_c provide evidence for the considerably greater stability (by ~7 kcal mol^{-1}) of one-centre adsorption forms in which imidazoline radicals are coordinated not *via* the NO group but *via* their second electron-donating position. The temperature dependences[5] of the shapes of the corresponding EPR spectra with their anisotropic splittings also point to these findings without ambiguity. The values of the complexation energies are indicative of the existence of strong hydrogen bonds.

In a quantum-chemical analysis of the experimentally investigated two-centre coordination of radicals **1** and **2** on the surface of partially dehydroxylated silica gel we have used four-model cluster constructions (CC) containing geminal (CC I) and vicinal (CC II) silanol groups as well as those separated by one (CC III) and two (CC IV) silicon-ox ygen tetrahedra. Applied to the optimization specified above the start geometry of each PSC studied was found to suggest the presence of two hydrogen bonds N···H–O–Si and N–O···H–O–Si, each with bond lengths of *ca.* 1.9 Å and 1.8 Å, respectively.

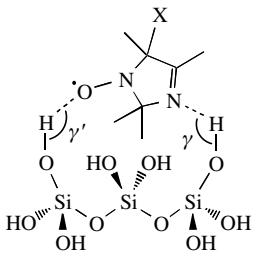
As our calculations by the MNDO method demonstrated, such two-centre coordination of imidazoline radicals **1** and **2** to the geminal silanol groups in CC I is energy-disfavoured (there is no minimum on the potential energy surface) and this is accounted for by purely geometric factors. Indeed, the spacing of the O and N(3) atoms in the radicals makes up around 3.5 Å, *i.e.* exceeds even twice the length of the Si–O bond. Thus, structural reasons for the most energy-favourable linear configurations of two hydrogen bonds are missing for these PSC.

The vicinal silanol groups of silica gel (CC II) are separated in space to a sufficient degree, and conclusions about their ability to form a two-centre nitroxyl PSC can be drawn merely on the basis of energetic criteria. Analogous calculations performed by us in this case also rule out the possibility of two-centre coordination of imidazoline radicals, since their assumed two-point adsorption forms convert in the course of full geometry optimization into a single-point one (γ = 180°) with bonding *via* the N(3) atom. Unless the lengths of both hydrogen bonds do not vary in these PSC but instead are taken as equal to the corresponding values in Table 1, such 'forced' two-centre coordination of radicals **1** and **2** at the vicinal silanol groups is energy-unfavourable by 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 (CC III) or two (CC IV) silicon–oxygen tetrahedra between the vicinal silanol groups moves the surface acid sites apart rather significantly. The structural, magnetic resonance, electrostatic and energy quantities calculated by the MNDO method which characterize the simultaneous coordination bonding of imidazoline radicals **1** and **2** with both acid sites of the model cluster $Si_3O_{10}H_8$ (Figure 2) and of its analogue $Si_4O_{13}H_{10}$ are shown in Table 2. Comparing the data

Table 2 Structural, magnetic resonance, electrostatic and energy characteristics of coordination of the imidazoline radicals with two acid sites of the model clusters $Si_3O_{10}H_8$ and $Si_4O_{13}H_{10}$.

Cluster	Radical	r(H··O)/Å	r[H···N(3)]/Å	θ/°	γ/°	γ'/°	φ/°	a^N_{iso}/G	$\rho^{N(1)}$	ρ^O	Q^R	|μ|/D	E_c/ kcal mol^{-1}
$Si_3O_{10}H_8$	**1**	1.82	1.93	58	179	176	12	22	0.54	0.46	0.27	6.8	–24.3
	2	1.86	1.96	60	178	178	14	22	0.55	0.44	0.28	6.5	–23.7
$Si_4O_{13}H_{10}$	**1**	1.83	1.93	55	180	177	13	22	0.55	0.45	0.27	7.2	–24.4
	2	1.86	1.97	57	179	178	14	22	0.55	0.43	0.27	7.0	–23.9



1 X = Me
2 X = Ph

Figure 2 Cluster two-centre PSC of imidazoline nitroxides with model acid site $Si_3O_{10}H_8$.

in Tables 1 and 2 it is easy to see that both hydrogen bonds H···O and H···N(3) in the two-centre PSC (Table 2) are somewhat longer than those in the corresponding one-centre PSC (Table 1), and in the case of the $Si_3O_{10}H_8$ cluster they assume slightly non-linear configurations (γ and γ' are not equal to 180°). This finding shows that there are small structural strains in such an adsorption form. At the same time, the degrees of pyramidality (φ) of the N(1) atom in the radicals **1** and **2** for single-point and two-point adsorption are very similar.

From a comparison of Tables 1 and 2 it is obvious that the isotropic hyperfine coupling constants $a_{iso}^{N(1)}$ and spin densities $\rho^{N(1)}$ and ρ^{O} of the N(1) and O atoms in the two-centre PSC (Table 2) are much the same as those in the one-centre PSC with binding through the O atom (Table 1). This is representative of the fact that the coordination of the imidazoline radicals *via* the N(3) atom yields little information on their structural, radiospectroscopic and electrostatic parameters.

It is important to note that even though the ratios of spin densities $\rho^{N(1)}$:ρ^{O} are inverted (Table 2) in comparison with those peculiar to the free radicals **1** and **2** (Table 1) the portions of spin transfer from O to N(1) are, however, smaller than in the case of one-centre coordination *via* the O atom. This gives evidence for the fact that the hydrogen bonds N–O···H–O–Si in the two-centre PSC are weaker than those in the one-centre PSC. Of particular interest is the fact that in the presence of two hydrogen bonds (Table 2) and in the absence of one of them (Table 1) the radical fragments in the model PSC have very similar positive charges Q^{R}.

According to the calculated energies of complexation E_c (Tables 1 and 2) the two-point adsorption of imidazoline radicals on the surface acid sites of silica gel must be much more favourable than the single-point one. The differences in the E_c values are an indication of the preference of the radicals **1** and **2** to be simultaneously coordinated *via* both their electron-donating sites rather than *via* a single N(3) atom. This difference is *ca.* 8 kcal mol^{-1} and is in good agreement with the experimentally established[5] enthalpies of transformation of slow-rotating imidazoline adsorption forms into fast-rotating ones. The insensitivity of the calculated radiospectroscopic and energy properties of PSC to the presence of a fairly voluminous phenyl substituent in the imidazoline ring also has experimental confirmation.[6]

The analysis of the $Si_4O_{13}H_{10}$ cluster structure shows that under two-point adsorption the cluster assumes a curved shape and the distance between the two silanol groups involved in the complexing is much the same as that in the short-cut analogue $Si_3O_{10}H_8$. The calculated characteristics of the coordination of these acid sites with radicals **1** and **2** (see Table 2) provide convincing evidence for the resemblance in geometries and electronic structures of paired acid sites in the 'minimal' ($Si_3O_{10}H_8$) and extended ($Si_4O_{13}H_{10}$) cluster quantum-chemical models.

Thus, the results of quantum-chemical analysis performed reveal that imidazoline nitroxides are capable of forming both one-centre and two-centre PSC with the differing acid sites of partially dehydroxylated silica gel. To judge by the calculated energies of complexing E_c, these radicals explicitly prefer (in the case of single-point adsorption) to be coordinated by such acid sites *via* the electron-donating position N(3) of the five-membered ring rather than *via* the NO group.

One must emphasize that $Si_3O_{10}H_8$ and $Si_4O_{13}H_{10}$ clusters allow 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 gel to be proposed. The $Si_3O_{10}H_8$ cluster is the smallest to be investigated with these aims in view, but enlargement of this cluster reveals that the insertion of extra silicon–oxygen tetrahedra does not invoke significant changes in the calculated adsorption characteristics. Less complex cluster constructions which contain only vicinal or, more often, geminal silanol groups are unsuitable for such calculations because the two-centre coordination of imidazoline radicals to the groups indicated is energy-inconsistent due to pronounced structural strains.

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