

Nitroxide radicals in studies of the fine bonded layer structure of modified silicas

Pavel G. Mingalyov, Alexander Yu. Fadeev*, Sergei M. Staroverov and Georgii V. Lisichkin

Laboratory of Petrochemical Synthesis, Chemical Department, Lomonosov State University, Len. Gory, 119899 Moscow (Russian Federation)

Elena V. Lunina

Laboratory of Adsorption, Chemical Department, Lomonosov State University, Len. Gory, 119899 Moscow (Russian Federation)

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ABSTRACT

Spin probe and spin label methods were applied in studies of the fine structure of both reversed-phase and functionalized modified silicas. The concept of a "rigid" structure for narrow-pore alkyl-modified silicas was experimentally supported. "Two-level" sorption of the solute in the bonded layer of end-capped alkyl-modified silicas was discovered. The stability of arch structures arising in the bonded layer of functionalized modified silicas was studied. It was shown that arch structures could be effectively destroyed in solvents with high basicity.

INTRODUCTION

Electron spin resonance (ESR) spectroscopy using paramagnetic probes and labels seems to be one of the most promising and informative techniques for the characterization of bonded layers of chemically modified silicas. The application of paramagnetic labels allows one to obtain important data on the organization of bonded molecules over the silica surface [1–6], the structure of bonded affinity ligands [7] and the dynamic behaviour of bonded molecules under various conditions [1,2,8–11].

Unfortunately, spin labelling in general leads to misrepresentation of the bonded layer structure and does not allow the study of some real

stationary phases. On the other hand, the paramagnetic probe method, unlike spin labelling, is more suitable for studying both the nature of the adsorption sites of an adsorbent and the behaviour of an adsorbate. The main advantages of the application of the spin probe method in surface science have been described in reviews [12,13].

This paper summarizes results obtained in our laboratory on the application of both spin probes and labels in the characterization of chemically modified silicas, which are widely employed as stationary phases in modern HPLC.

EXPERIMENTAL

Synthesis of reversed-phase bonded silicas

Modification of the initial silicas was carried out using trichloro- and monochlorosilanes. A

* Corresponding author.

portion of sample was end-capped with a mixture of trimethylchlorosilane and hexamethyl-disilazane (1:1). Modification and end-capping were done as described elsewhere [14–16] using anhydrous toluene as a solvent and pyridine as an activator.

Adsorption of a spin probe

Adsorption of 2,2,6,6-tetramethylpiperidone-4-oxyl-1 (TEMPO) and 2,2,6,6-tetramethyl-4-aminopiperidine-1-oxyl (TEMPO-Amine) was carried out from dilute diethyl ether solutions with further evaporation of the solvent *in vacuo*. The amount of adsorbed radical (m_r) was varied from 0.007 to 0.049 mmol/g. The surface concentration of adsorbed radicals (C_r) was calculated as [17–19]

$$C_r \text{ (mmol/m}^2\text{)} = m_r/S_r \quad (1)$$

where S_r is the surface area accessible to 2,2,6,6-tetramethylpiperidone-4-oxyl-1, calculated as [17–19]

$$S_r = S_{\text{BET}}(\sigma_r/\sigma_{\text{benz}})^{(2-d)/2} \quad (2)$$

where S_{BET} is the specific surface area determined by benzene adsorption, σ_{benz} and σ_r are the adsorptional areas of benzene and radicals on silica, 0.49 [20] and 1.21 m² [21], respectively, and d is the surface fractal dimension of the silicas used: $d = 2.0$ for S-80, S-120 and Li-500, 2.3 for A-300, 2.6 for Si-100 and Si-60 and 2.8 for Si-600 [19].

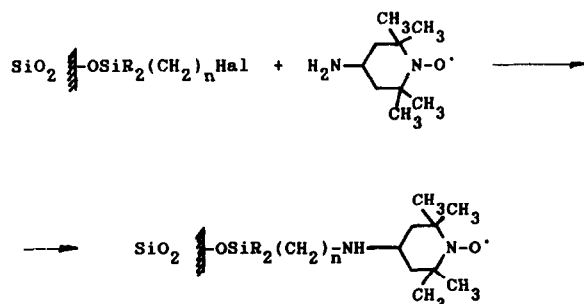
Synthesis of ω -haloalkyl-bonded silicas

Modification of the initial silicas was carried out using ω -haloalkylchlorosilanes, $\text{ClR}_2\text{Si}(\text{CH}_2)_n\text{Hal}$, as modifiers: $n = 1$ and 3, $\text{R} = \text{CH}_3$, $\text{Hal} = \text{Br}$ and $n = 11$, $\text{R} = \text{Cl}$, $\text{Hal} = \text{Cl}$. The latter sample was end-capped with trimethylchlorosilane.

The procedure for modification was as follows: 1 g of vacuum-dried silica was stirred in boiling anhydrous toluene containing 1 mmol of modifier for 10 h, then the sorbents were washed consecutively with anhydrous toluene, toluene, acetone, acetone–water (1:1) and acetone and subsequently washed in a Soxhlet apparatus with diethyl ether for 6 days.

Spin labelling

2,2,6,6-Tetramethyl-4-aminopiperidine-1-oxyl was attached to the modified silicas via the following reaction:



A 1-g amount of ω -haloalkyl-bonded silica was stirred with absolute dimethylformamide containing 1 mmol of label and 1 mmol of *N,N*-diisopropylethylamine for 3 h at 80–90°C. The labelled sorbents were washed consecutively with acetone, distilled water, saturated NaHCO_3 solution and distilled water and then washed in a Soxhlet apparatus with acetone–water (1:1) for 2 days.

ESR measurements

Measurements were made with an RE-1307 ESR spectrometer. Dry sample was placed in a glass tube and evacuated to a pressure of 0.01 Torr (1 Torr = 133.322 Pa). The sample covered with a solvent was placed in a glass tube, frozen with liquid nitrogen and evacuated to a pressure of 0.01 Torr. The correlation time τ_c was determined in accordance with published methods [22,23].

A_{\parallel} was determined from the ESR spectra as described [22,23]. The isotropic g -factor was obtained using diphenylpicrylhydrazyl as internal standard. The total amount of both immobilized and adsorbed radicals was determined by integrating the ESR spectra.

Determination of bonding density

Bonding densities of attached molecules were calculated from the carbon analysis data and specific surface area [24,25].

Determination of specific surface area

Specific surface area was determined by benzene adsorption [20].

RESULTS AND DISCUSSION

Modelling of behaviour of an adsorbate on the reversed-phase bonded silica surface

Effects of alkyl chain length, type of anchor group and end-capping. The radical used (2,2,6,6-tetramethylpiperidone-4-oxyl-1) seems to be suitable for probing various adsorption sites on reversed-phase bonded silicas. Indeed, this probe can interact both with bonded alkyl groups via Van der Waals's forces and specifically with residual silanol groups. As a measure of the probe mobility the correlation time τ_c was chosen. This value is the reciprocal of the radical rotation frequency [23] and can easily be obtained from ESR spectra.

The characteristics of the sorbents under study are presented in Table I. To avoid the effect of surface concavity, wide-pore silicas were used.

The synthesized sorbents may be classified into four groups on the basis of the functionality of the silane used and end-capping.

(I) The first group consists of sorbents modified with trichlorosilanes (Table I, Nos. 1–3). When adsorbed on such samples, the probe shows only a slow rotation mode in the ESR spectra (Table II). This seems to be connected with the strong specific interaction between the probe and silanol groups (Fig. 1A). The latter have been shown to exist on the surface in large amounts after hydrolysis of non-reacted Si–Cl groups [14,15,26]. It should be emphasized that “rapid” rotation of probes does not occur even at 130°C.

Thus, accessible silanol groups obviate the role of Van der Waals interactions between an adsorbate

TABLE I
CHARACTERISTICS OF THE MODIFIED SILICAS STUDIED

No.	Initial silica	Modifier	Specific surface area (m ² /g)	Average pore diameter (nm)	Carbon percentage	Bonding density ^a (μmol/m ²)	End-capping	Designation
1	Silokhrom (S-80)	C ₈ H ₁₇ SiCl ₃	67	50	1.8	2.50	–	C ₈ T
2	S-80	C ₁₂ H ₂₅ SiCl ₃	67	50	4.0	3.66	–	C ₁₂ T
3	S-80	C ₁₈ H ₃₇ SiCl ₃	67	50	5.5	3.66	–	C ₁₈ T
4	S-80	(CH ₃) ₃ SiCl	67	50	1.3	3.83	–	C ₁ M
5	S-80	<i>t</i> -C ₄ H ₉ SiMe ₂ Cl	67	50	2.0	3.66	–	<i>t</i> -C ₄ M
6	LiChrosorb (Li-500)	C ₄ H ₉ SiMe ₂ Cl	90	50	2.7	3.83	–	C ₄ M
7	Li-500	C ₆ H ₁₃ SiMe ₂ Cl	90	50	3.0	3.66	–	C ₆ M
8	Armsorb A-300	C ₁₆ H ₃₃ SiMe ₂ Cl	166	25	10.3	3.33	–	C ₁₆ M
9	S-80	C ₈ H ₁₇ SiCl ₃	67	50	2.0	2.50	+	C ₈ T/s
10	S-80	C ₁₂ H ₂₅ SiCl ₃	67	50	4.1	3.66	+	C ₁₂ T/s
11	A-300	C ₁₆ H ₃₃ SiCl ₃	166	25	10.6	3.50	+	C ₁₆ T/s
12	S-80	C ₁₈ H ₃₇ SiCl ₃	67	50	5.6	3.66	+	C ₁₈ T/s
13	Li-500	C ₄ H ₉ SiMe ₂ Cl	90	50	2.7	3.83	+	C ₄ M/s
14	Li-500	C ₆ H ₁₃ SiMe ₂ Cl	90	50	3.0	3.66	+	C ₆ M/s
15	S-80	C ₁₆ H ₃₃ SiMe ₂ Cl	67	50	5.0	3.66	+	C ₁₆ M/s
16	Silasorb Si-100	C ₁₆ H ₃₃ SiMe ₂ Cl	283	11.3	15.3	3.25	–	C ₁₆ /Si-100
17	Silasorb Si-60	C ₁₆ H ₃₃ SiMe ₂ Cl	213	10.5	10.9	2.90	–	C ₁₆ /Si-60
18	Silasorb Si-600	C ₁₆ H ₃₃ SiMe ₂ Cl	476	5.4	17.6	2.24	–	C ₁₆ /Si-600

^a Determined before end-capping.

TABLE II

EFFECT OF TYPE OF MODIFIER ON STATE OF THE PROBE ADSORBED IN THE BONDED LAYER

No.	Designation ^a	Probe concentration (mmol/g)	Correlation time τ_c (s)		Activation energy of rotation (kJ/mol)	Log of dispersion of probe distribution on correlation time	
			20°C	136°C		20°C	136°C
<i>Modifier RSiCl₃, probe TEMPO</i>							
1	C ₈ T		$1.5 \cdot 10^{-8}$	$5 \cdot 10^{-9}$	9.1		
2	C ₁₂ T		$2 \cdot 10^{-8}$	$5 \cdot 10^{-9}$	12.9		
3	C ₁₆ T		$2 \cdot 10^{-8}$	N.d. ^b	N.d.		
<i>Modifier RSiMe₂Cl, probe TEMPO</i>							
4	C ₁ M	0.0067	$5 \cdot 10^{-9}$	$2.5 \cdot 10^{-9}$	5.1	1	1
5	<i>t</i> -C ₄ M	0.0067	$2 \cdot 10^{-8}$	$3.9 \cdot 10^{-9}$	11.2	1	1
6	C ₄ M	0.0090	$2 \cdot 10^{-8}$	$3.2 \cdot 10^{-9}$	14.4	1	1
7	C ₆ M	0.0090	$1 \cdot 10^{-8}$	N.d.	N.d.	1	N.d.
8	C ₁₆ M	0.0067	$2 \cdot 10^{-8}$	$7 \cdot 10^{-9}$	N.d.	1	4
8	C ₁₆ M	0.0110	$1 \cdot 10^{-8}$	N.d.	N.d.	2	N.d.

^a According to Table I.^b Not determined.

bate and attached chains and completely define the state of adsorbed molecules. It is noteworthy that an analogous result was obtained earlier for fluorescent probes adsorbed on alkylated silicas [19,27].

(II) Sorbents modified with monochlorosilanes belongs to the second group (Table I, Nos. 4–8). The adsorbed probe, like that on the trichlorosilane-modified silicas, shows only a slow rotation mode at room temperature. For long-chain silicas an increase in temperature leads to a substantial increase in the dispersion of the radical distribution with their correlation times. An analogous effect also takes place as the probe concentration increases (Table II).

The observed phenomena are probably connected with the weaker “adsorbate–silanol

group” interaction compared with that for silicas modified with trichlorosilanes. The weakest hydrogen bonds are evidently destroyed on increasing the temperature. On the other hand, the amount of comparatively strong hydrogen bonds is limited and an increase in probe concentration leads to an increase in weaker hydrogen bonds. We assume that these effects result in polydispersity of adsorption states.

(III) The third group contains sorbents modified with trichlorosilane and further end-capped (Table I, Nos. 9–12). End-capping is known to change considerably the bonded layer structure of modified silicas [14,15]. First, end-capping shields surface silanol groups and therefore increases markedly the hydrophobicity of the bonded layer [8,19,28–30]. Second, the chain mobility was found to decrease after end-capping. This was ascribed to association between alkyl chains and trimethylsilyl groups [31]. Spin-lattice relaxation time measurements on the ¹³C NMR signals also showed that the mobility of bonded alkyl chains decreases after end-capping [26,32].

The above features of end-capped samples must influence the behaviour of adsorbed probes. Indeed, for the samples obtained using

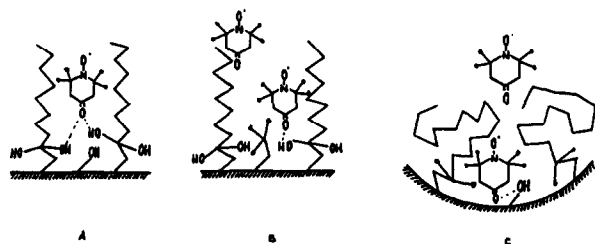


Fig. 1. Various states of probe adsorbed in the bonded layer.

long-chain trichlorosilanes and further end-capped, one can observe two different adsorption states: “rapidly” and “slowly” rotating probes (Table III). This may be connected with the “loosening” of the bonded layer due to bulky trimethylsilyl attached groups (Fig. 1B). Rapidly rotating probes are adsorbed in the upper part of the bonded layer and interact with bonded alkyl chains only by Van der Waals’s forces. On the other hand, the slow type of rotation is inherent in probes which are specifically adsorbed on residual silanol groups. It was shown that the number of accessible silanol groups is limited. Hence increasing the probe loading results in an increase in the proportion of rapid rotation. Increasing the temperature also leads to an increase in the proportion of rapid rotation (Table III).

The observed results show that specific interaction of the probe with the surface is weaker

than for non-end-capped samples. Hence end-capping of silicas modified with trichlorosilanes shields residual silanol groups, although the total shielding could hardly be achieved in this way.

(IV) Greater shielding of the silica surface can be achieved using monochlorosilanes with further end-capping (Table I, Nos. 13–15). On these samples the proportion of rapid rotation is three to four times greater than that one for samples modified with trichlorosilanes at room temperature and the value even reaches 100% at 100°C (Table III). It is remarkable that such an effect of “two-level” sorption is so sharply pronounced only for long bonded chains (more than eight carbon atoms). The proportion of rapidly rotating probes decreases as the chain length is decreased and for short-chained samples the value reaches zero (Table III).

Effect of the support pore diameter. In our previous theoretical [25,33] and experimental

TABLE III
EFFECT OF END-CAPPING ON STATE OF THE PROBE ADSORBED IN THE BONDED LAYER

<i>Modifier RSiCl₃/end-capped</i>								
No.	Designation ^a	Probe	Correlation time τ_c of “slow” form (s)		Proportion of “slow” form (%)		Correlation time τ_c of “rapid” form (s)	
			20°C	92°C	20°C	92°C	20°C	92°C
9	C ₈ T/s	TEMPO	2 · 10 ⁻⁸	5 · 10 ⁻⁹	70	70	5 · 10 ⁻⁹	1 · 10 ⁻⁹
10	C ₁₂ T/s	TEMPO	2 · 10 ⁻⁸	1 · 10 ⁻⁸	50	50	2 · 10 ⁻⁹	1 · 10 ⁻⁹
11	C ₁₆ T/s	TEMPO	2 · 10 ⁻⁸	1 · 10 ⁻⁸	90	70	1 · 10 ⁻¹⁰	1 · 10 ⁻¹¹
12	C ₁₆ T/s	TEMPO-Amine	2 · 10 ⁻⁸	N.d. ^b	ca. 100	N.d.	N.d.	N.d.
	C ₁₈ T/s	TEMPO	2 · 10 ⁻⁸	N.d.	85	N.d.	1 · 10 ⁻¹⁰	N.d.

Modifier RSiMe₂Cl/end-capped, probe TEMPO

No.	Designation ^a	Probe concentration (mmol/g)	Correlations time τ_c of “slow” form (s)		Proportion of “slow” form (%)		Correlation time τ_c of “rapid” form (s)		Activation energy of rotation (kJ/mol)
			20°C	136°C	20°C	136°C	20°C	136°C	
13	C ₄ M/s	0.009	3 · 10 ⁻⁹	1.5 · 10 ⁻⁹	100	100	—	—	10.7
14	C ₆ M/s	0.009	1 · 10 ⁻⁸	5 · 10 ⁻⁹	ca. 100	95	N.d.	1 · 10 ⁻⁹	N.d.
15	C ₁₆ M/s	0.007	1 · 10 ⁻⁸	—	60	0	1 · 10 ⁻⁹	1 · 10 ⁻⁹	15.4

^a According to Table I.

^b Not determined.

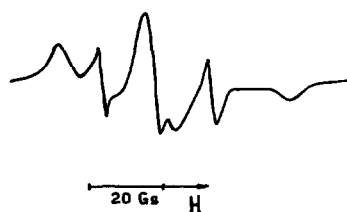


Fig. 2. ESR spectrum of TEMPON adsorbed on Si-600 hexadecyldimethylchlorosilane-modified silica. Surface concentration of TEMPON = 0.130 nm^{-2} .

[19] studies it was shown that the conformational structure of bonded layers formed with long alkyl chains depends considerably on the initial support pore diameter. A decrease in the average pore diameter reduces the bonded layer of the "rigid" structure in contrast to the "flexible" structure found in wide-pore silicas. This section considers the effect of the initial silica pore diameter on the nature of the adsorption states in the bonded layer of silicas modified with hexadecyldimethylchlorosilane. The characteristics of the samples used are presented in Table I, Nos. 16–18.

The behaviour of a probe adsorbed on narrow-pore silicas modified with hexadecyldimethylchlorosilane differs drastically from that on wide-pore sorbents. First, one can observe two-level adsorption for all the samples studied, but the

correlation time for slow radicals is 10^4 times greater than τ_c for rapid radicals (Fig. 2). This ratio is 100 times greater than for the wide-pore samples (Table IV). Second, unlike the wide-pore silicas modified with monochlorosilanes without end-capping, the proportion of rapid radicals increases as the probes loading increases. Third, increasing the temperature to 130°C does not result in an increase in the dispersion of the radical distribution on their correlation times.

The observed phenomena could be explained in the framework of the rigid structure concept [25,34]. Indeed, at low concentrations of the probe adsorption occurs on the residual silanol groups under interlaced bonded alkyl chains. Molecules of adsorbate are surrounded by bonded chains on one side and with the surface on the other. The probe is as if it were in a "molecular closet" (Fig. 1C).

Rotational activation energy values of slow radicals are given in Table IV. The values increase as the pore diameter decreases, and therefore as the proportion of rigid structure increases [34]. The observed values are greater than those of probes adsorbed both on pure silica and on modified wide-pore silicas.

Increasing the amount of the probe leads to the appearance of probes adsorbed on the

TABLE IV

EFFECT OF AVERAGE SILICA SUPPORT PORE DIAMETER ON STATE OF THE PROBE ADSORBED IN THE BONDED LAYER OF HEXADECYLDIMETHYLCHLOROSILANE-MODIFIED SILICAS

No.	Modified silica ^a	Average pore diameter (nm)	Concentration of probe ^b (nm^{-2})	τ_c of "slow" form (s)		Proportion of "slow" form (%)	τ_c of "rapid" form at 20°C (s)	Activation energy of rotation (kJ/mol)
				20°C	136°C			
16	C ₁₆ /Si-100	11.3	0.074	$1.6 \cdot 10^{-8}$	$2 \cdot 10^{-9}$	100	—	17.9
16	C ₁₆ /Si-100	11.3	0.120	$1.6 \cdot 10^{-8}$	N.d. ^c	ca. 100	N.d.	N.d.
17	C ₁₆ /Si-60	10.5	0.074	$1.7 \cdot 10^{-8}$	$2 \cdot 10^{-9}$	100	—	18.0
17	C ₁₆ /Si-60	10.5	0.120	$1.6 \cdot 10^{-8}$	N.d.	ca. 100	N.d.	N.d.
18	C ₁₆ /Si-600	5.4	0.013	$3.2 \cdot 10^{-8}$	$1.8 \cdot 10^{-9}$	100	—	24.0
18	C ₁₆ /Si-600	5.4	0.080	$3.2 \cdot 10^{-8}$	N.d.	ca. 100	N.d.	N.d.
18	C ₁₆ /Si-600	5.4	0.130	$1 \cdot 10^{-7}$	N.d.	95	$1 \cdot 10^{-11}$	N.d.
18	C ₁₆ /Si-600	5.4	0.080	$3.2 \cdot 10^{-8}$	N.d.	100	—	N.d.

^a According to Table I.

^b First seven entries, probe = TEMPON; bottom entry, probe = TEMPO-Amine.

^c Not determined.

bonded layer. These radicals are hardly dissolved in the bonded layer as they are too mobile.

It is paradoxical, but the probes adsorbed on the bonded layer at room temperature have the same mobility as those adsorbed in the “upper” part of the bonded layer of wide-pore silicas at 130°C. At the same time, the probes adsorbed “under” the bonded layer behave as if they are frozen by liquid nitrogen!

Effect of the nature of the adsorbate. This section considers the effect of the nature of the adsorbate on its behaviour. Two nitroxide radicals containing keto (TEMPO) or amino groups (TEMPO-Amine) were selected as adsorbates (see Experimental).

These radicals have different capabilities of forming hydrogen bonds with surface silanols. The presence of a primary amino group in the probe molecule increases markedly the specific interaction between the probe and the silica surface. Indeed, TEMPO-Amine, unlike TEMPO, virtually does not “sense” end-capping of the sorbents. The proportion of rapidly rotating probes for TEMPO-Amine adsorbed on the end-capped alkyl-modified silicas is almost zero, whereas for TEMPO this value is about 10% (Table III).

On the sorbents with a rigid structure of the bonded layer the rapidly rotating probes in the case of TEMPO appear at a lower loading than those for TEMPO-Amine (Table IV). Hence the effectiveness of surface shielding depends considerably on the nature of the adsorbate. We consider that the “total” shielding of the surface of the modified silicas is hardly possible, especially for adsorbates such as amines.

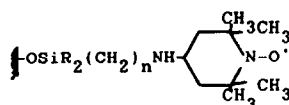
Formation–destruction of hydrogen bonds in bonded layers of functionalized silicas

Functionalized silica sorbents are as commonly used as reversed phases in modern liquid chromatography. They are various stationary phases for normal-phase, ion-exchange, ligand-exchange, affinity and other chromatographic modes [15,24,35].

Bonded functional groups are known to form cyclic structures with the silanol groups of the silica surface [15,24]. These are often referred to as “arch” structures. Various arch structures have

been studied using NMR [36–39] and IR spectrometry [37,40–43] and titrimetric [44], adsorption [45] and liquid chromatographic techniques [46]. In this work, the application of spin labels allowed us to observe directly the processes of formation and destruction of arch structures under various conditions.

Behaviour of spin labels on dry sorbents. The following spin-labelled modified silicas were used:



where $R = \text{CH}_3$, $n = 1$ and 3 or $R = \text{Cl}$, $n = 11$, designated C_1 , C_3 and C_{11} , respectively. The last sample was end-capped.

Without a solvent, immobilized radicals have a correlation time of *ca.* 10^{-8} s. Such a high value of τ_c confirms the strong interaction between the amino groups of the modifier and the silanol groups of the silica surface. Indeed, the correlation times of radicals that are immobilized on a non-specific surface can reach 10^{-10} s at the same temperature [47].

We assumed the formation of arch structures either by amino groups of the modifier or by nitroxyl groups of label (Fig. 3). Apparently both types of arch structures are present on the surface. However, the contribution of amino groups decreases as the spacer length is decreased. Indeed, A_{\parallel} increases from C_1 to C_{11} (Table V), and for C_1 samples it corresponds to that usually observed when nitroxide groups forms hydrogen bonds with surface silanols [12]. Thus, according to [23,48–50], on the basis of the absolute values of A_{\parallel} one can say that the polarity of the bonded layer decreases as the

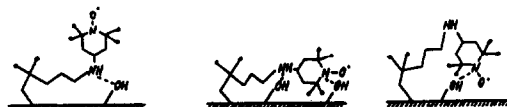


Fig. 3. Possible types of arch structures on modified silicas.

TABLE V

EFFECT OF SPACER LENGTH ON THE STATE OF THE BONDED SPIN LABEL

Spacer length (C atoms)	τ_c (s)		Proportion of "rapid" form (%)		g -Factor	$A_{ }$ (G)
	20°C	83°C	20°C	83°C		
	1	$2 \cdot 10^{-8}$	$8 \cdot 10^{-9}$	0		
3	$2 \cdot 10^{-8}$	$6 \cdot 10^{-9}$	0	0	2.0055	36.2
11	$2 \cdot 10^{-8} + 2 \cdot 10^{-9}$	$1 \cdot 10^{-8} + 5 \cdot 10^{-10}$	5	5	2.0057	35.5

spacer length increases. The increase in the g -factor from C_1 to C_{11} also confirms this tendency [51,52].

It was unexpected that arch structures could not be destroyed up to 83°C (Table V).

Effect of solvent on stability of arch structures. Series of solvents having approximately the same viscosity but different dielectric permeability (ϵ) and basicity function (B) according to Palm [54] were chosen. The characteristics of the solvents used are given in Table VI.

Effect of solvent dielectric permeability. There are two possibilities of destroying an arch structure in the presence of a solvent (Fig. 4). If arch structures were destroyed forming ion pairs (Fig. 4, top), this process would be markedly facilitated in solvents with a high dielectric permeability. However, for all the samples studied a sixfold increase in dielectric permeability from ethyl acetate to acetonitrile did not lead to an increase in the proportion of rapid radicals.

TABLE VI

CHARACTERISTICS OF THE SOLVENTS EMPLOYED

Solvent	η (mPs) [53]	ϵ [53]	B [54]
Carbon tetrachloride	9.7	2.2	0
Bromobenzene	9.9	5.4	40
Nitromethane	6.1	38.6	65
Acetonitrile	3.45	36.2	160
Ethyl acetate	4.41	6.02	181
Ethanol	9.45	12.3	229
Pyridine	10.8	24.3	472

Hence the destruction of arch structures occurs without the formation of ion pairs.

Effect of solvent basicity. The ease of destruction of arch structures without the formation of ion pairs (Fig. 4, bottom) must increase as the solvent basicity (B) [54] increases. However, this dependence is complicated (Figs. 5–7).

The observed stepped character of these diagrams is probably connected with the consequent destruction of hydrogen bonds. The weakest hydrogen bonds, corresponding to nitroxyl groups, are destroyed first. Then more stronger hydrogen bonds, formed by more basic amino groups, are destroyed. However, for the sample with the shortest spacer there is only one step on the diagram. This is evidently connected with the impossibility of hydrogen bond formation between amino and silanol groups because the spacer is too short.

The proportion of rapid radicals increases as

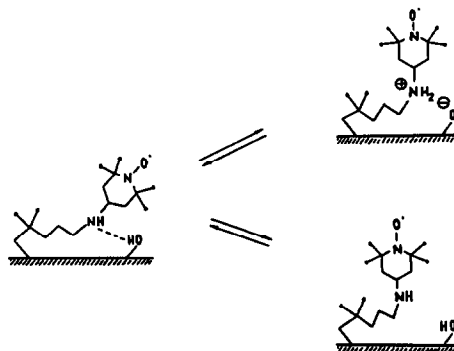


Fig. 4. Possible mechanisms of destruction of arch structure.

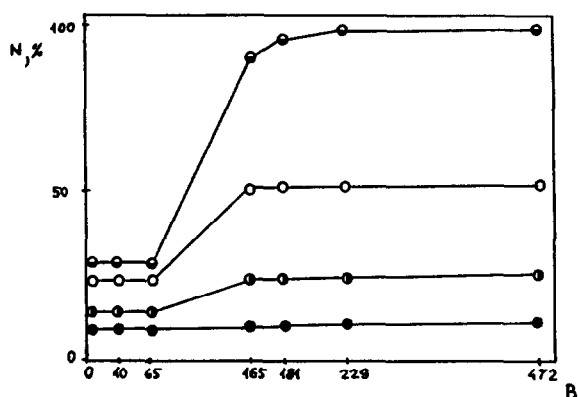


Fig. 5. Proportion of "rapid" radicals on solvent Palm basicity function for sample C_1 . ● = 28°C; ◐ = 53°C; ○ = 70°C; ◑ = 83°C.

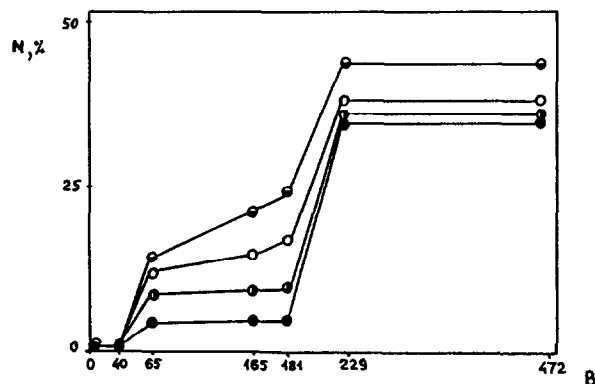


Fig. 6. Proportion of "rapid" radicals on solvent Palm basicity function for sample C_3 . ● = 28°C; ◐ = 53°C; ○ = 70°C; ◑ = 83°C.

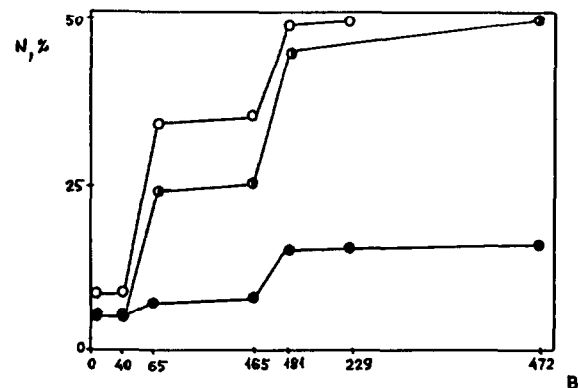
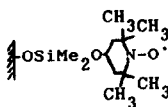


Fig. 7. Proportion of "rapid" radicals on solvent Palm basicity function for sample C_{11} . ● = 28°C; ◐ = 53°C; ○ = 70°C.

the temperature increases, unlike for the dry samples.

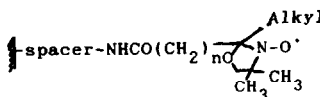
It is interesting that the strength of the arch structure formed by amino groups for C_{11} is lower than that for C_3 . Indeed, the latter is destroyed in solvents with a lower B (Figs. 6 and 7). We consider that this may be connected with the more shielded surface due to the end-capping procedure and long hydrophobic spacer.

Here we discuss our own results and literature data on the strength of the arch structure in the presence of a solvent. Gilpin *et al.* [9] studied the following nitroxide label:



Arch structures were found to be stable in non-basic solvents (aliphatic hydrocarbons, $B = 0$, and toluene, $B = 58$ [54]). However, they were destroyed in *n*-butanol, $B = 234$, 2-propanol, $B = 240$, and *tert.*-butanol, $B = 247$ [54].

Sistovaris *et al.* [2] studied nitroxide labels bonded to silica surface via various spacers:



It was shown that in the presence of methylene chloride ($B = 23$) the mobility of the bonded label had increased as much as if the label had been dissolved in a common solvent. However, it was observed only for samples that contained nitroxyl fragments located far from the amido group (ten or even fourteen methylene groups). In addition, nitroxyl fragments were shielded strongly with alkyl groups situated in an α -position with respect to the nitroxyl groups. Here one finds that, first, a hydrogen bond formed between such a nitroxyl group and the surface is less strong than that observed in our study. Second, one can hardly say anything about the arch structure formed between silanol groups and amido groups. Indeed, the amido groups are too far from the nitroxyl groups. Anyway, arch

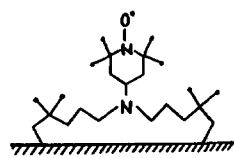


Fig. 8. Doubly alkylated label on silica surface.

structures formed by amino groups are stronger than those formed by either amido or nitroxyl groups (typical values of B for amides are 250–350 and for amines 600–700 [54]).

It should be noted that even in such basic solvents as pyridine and ethanol about 50% of the labels are in the slow form (Figs. 6 and 7). We assume that immobilization of 2,2,6,6-tetramethyl-4-aminopiperidine-1-oxyl yields both singly and doubly alkylated labels. Multi-site alkylation of immobilized ligand occurs with high concentrations of surface-bonded reactive groups and a comparatively low loading of ligand [7,55–57].

Doubly alkylated labels can hardly possess enough rotational mobility (Fig. 8). On the other hand, the double alkylation evidently is impossible for samples with a short spacer owing to steric hindrance.

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