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The Paramagnetic Probe Method in Adsorption and Catalysis

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The application of the paramagnetic probe method to studies of heterogeneous systems is discussed. By analysing the ESR spectra of the adsorbed probes (nitroxyl radicals) information is obtained on the interaction of the probe with the surface of silica gel, aluminium oxide, alumina-silicas, etc. Special attention is paid to the formation of donor-acceptor complexes with co-ordinationally unsaturated cations of the surface, and to the mobility of molecules in the adsorption layer. 53 references

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I. INTRODUCTION

The fundamental problems in adsorption and catalysis are the formation of the adsorption layer, the nature and the number of adsorption and catalytically active centres, the type of interaction between these centres and the adsorbed molecules, and the dynamics of the adsorption layer. Significant progress towards the solution of these problems has been made by using spectroscopic methods, and in particular the ESR method. The latter method is widely applied in studies of catalysts containing paramagnetic ions and radiation-induced defects as active centres, and also in studies of the interaction of various molecules with these centres and of the radical and ion-radical states created by the interaction of some adsorbates with the active surface of solids[1,2].

The paramagnetic probe method has been used in recent years to study catalysts and adsorbents which do not contain paramagnetic centres, in particular very commonly used materials such as alumina and some other oxides, alumina–silicas, and zeolites. The method consists in adding to the system paramagnetic particles (probes) and monitoring their ESR spectra, whose changes reflect the properties of the environment which the probes experience. In this review we shall be concerned mainly with the results obtained by using stable nitroxyl radicals as probes. The theory of the ESR spectra of these radicals is adequately developed[3,4], and by analysing the ESR spectra of adsorbed nitroxyl radicals we can study the interaction of these particles with the surface adsorption centres and in many cases we can observe the adsorption centres directly. Equally important is the possibility of measuring the velocity of the rotational and translational motion of the adsorbed molecules, i.e. of studying the dynamics of the adsorption layer.

Nitroxyl radicals offer a convenient model of adsorbates of the donor type. They all contain the $>$N–O fragment, which includes an unpaired electron as well as having normal donor properties. In addition to the $>$N–O group the radicals may contain other donor groups able to interact specifically with the active centres of the adsorbent. The presence of an unpaired electron allows the behaviour of these molecules in the adsorption layer to be monitored by ESR but does not otherwise affect the adsorption. Therefore studies of adsorption processes by the paramagnetic probe method are qualitatively applicable to a large number of adsorbates widely used in industry.

II. INTERACTION OF NITROXYL RADICALS WITH THE SURFACE OF OXIDE CATALYSTS

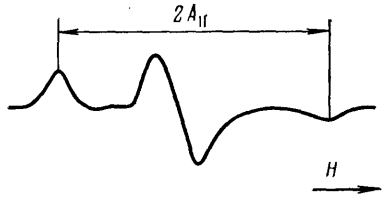
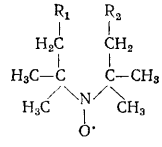
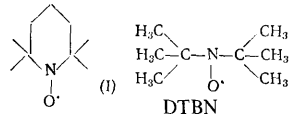


Figure 1. Determination of the anisotropy constant for the hyperfine interaction of an unpaired electron with the ^{14}N nucleus ($A_\parallel$) in the ESR spectra of randomly oriented "frozen" nitroxyl radicals[5].

The ESR spectrum of nitroxyl radicals, which include the fragment



for example, 2,2,6,6-tetramethylpiperidine-1-oxyl (I) or di-t-butylnitroxyl (DTBN)



(I) DTBN

consists of three hyperfine structure (HFS) components due to interaction of the unpaired electron with the ^{14}N nucleus (nuclear spin $I_N = 1$). The anisotropy constant $A_\parallel$ of the hyperfine interaction (HFI) of the unpaired electron with the ^{14}N nucleus (Fig.1) is a function only of the electron spin density on the nitrogen atom. If the $>$N–O group takes part in any interaction, for example by forming a donor–acceptor or a hydrogen bond, the electron spin density

on the nitrogen atom changes, and $A_{\parallel}$ also changes[4,6]. This effect is illustrated in Table 1. When these interactions are absent or insignificant, as in solutions in non-polar solvents or in pyridine frozen to a glass at 77 K, $A_{\parallel}$ amounts to 34–35 Oe. Hydrogen bond formation raises $A_{\parallel}$ to 38 Oe, and protonation to almost 40 Oe.

Table 1. *A* values (Oe) for the ESR spectra of nitroxyl radicals in different systems.

System	DTBN (Ref.6)	Radical (I) (Ref.7)
Glassy matrix		
n-Hexane	34.1	—
Toluene	34.6	34.6
Pyridine	35.2	35.3
Aqueous glycerol	—	37.8
Phenol	38.3	—
H_3PO_4 (10–40%)	—	39.5
Adsorption on silica gel		
Clean surface	38.6	38.0
Sample immersed in toluene	—	38.0
Adsorbed monolayer of pyridine	—	36.2
Sample immersed in pyridine	35.2	—

The interaction of the radicals (I) and DTBN with SiO_2 and hydroxylated Al_2O_3 surfaces has been found to give a high (38 Oe) value of the constant $A_{\parallel}$, characteristic of the formation of hydrogen bonds with the surface OH groups. The result was not unexpected, since hydrogen bond formation between donor molecules and the surface OH groups had been observed by i.r. spectroscopy[8]. However, the ESR method can be used to monitor changes in the interaction between radicals and surfaces resulting from the adsorption of other substances. This feature is very important because optical spectroscopic methods do not usually give this information.

An excess of non-polar molecules (toluene, CCl_4) does not affect the bond between radical (I) and the OH groups of the surface ($A_{\parallel}$ is unchanged), but donor molecules (for example, pyridine) can displace the radicals from the surface OH groups by being competitively adsorbed, as shown by changes in the $A_{\parallel}$ constant. Thus, when the surface is covered with a monolayer of pyridine the $A_{\parallel}$ value of radical (I) is 36.2 Oe. The displaced radical evidently interacts with polar elements of the surface structure, since the $A_{\parallel}$ constant remains higher than for non-polar solvents. We shall arbitrarily regard the radicals displaced from specific adsorption centres as physisorbed.

Sistovaris and coworkers[9] investigated the interaction of various nitroxyl radicals with a modified silica gel surface by analysing changes in the $A_{\parallel}$ parameter.

However, information on the nature of the adsorption centre can be obtained not only through measurements of $A_{\parallel}$. Complex formation between the >N–O group and Lewis acids with cations having non-zero nuclear spin can give rise to an additional hyperfine structure in the ESR spectra[10–12]. On γ-Al_2O_3 (activation temperature $T_a > 150$ °C) the radical (I) forms a bond with the acceptor centres (coordinationally unsaturated Al^{3+} ions) to give a surface complex with the >N–O→Al< structure[13]. The ESR spectrum of this complex contains components from the interaction of the unpaired electron with the ^{27}Al nucleus ($I_{Al} = 5/2$, Fig. 2*a*). This spectrum is fully analogous to the spectrum of the complex between the radical (I) and $AlCl_3$ in a glassy toluene solution (Fig. 2*b*).

Similar spectra for the complex between radical (I) and the acceptor centres have been observed not only on Al_2O_3 but also on alumina–silicas, fluorinated alumina[11], type HY zeolite[14] (in all of which the complex is formed with the Al^{3+} ion), and on Ga_2O_3 (complex with the Ga^{3+} ion). Thus the radical (I) acts as a selective indicator of centres of this type. This is one of the few instances of direct spectroscopic observation of the adsorption centre itself.

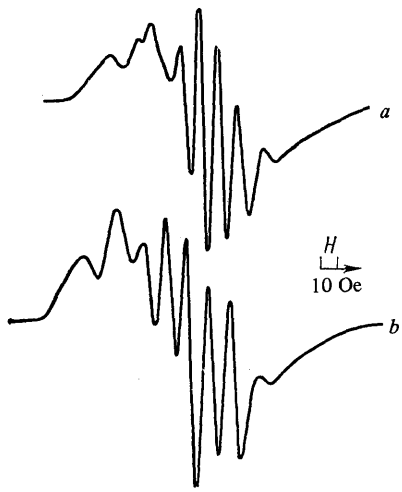


Figure 2. ESR spectra of the nitroxyl radical (I):[11] (*a*) complexed with the coordinationally unsaturated Al^{3+} ions of activated γ-Al_2O_3 at 20 °C; (*b*) complexed with $AlCl_3$ in toluene at −110 °C.

The ESR spectra of the complex with the coordinationally unsaturated Al^{3+} ion have been observed also with DTBN used as the paramagnetic probe[6]. By modelling the experimental spectra on a computer the authors were able to show that the constants of the anisotropic hyperfine interaction with the ^{14}N and ^{27}Al nuclei are somewhat different for different catalysts (Table 2). The differences are ascribed to the difference in strength of the acceptor centres of these catalysts.

Table 2. Anisotropic hyperfine interaction constants (Oe) of an unpaired electron with the ^{14}N and ^{27}Al nuclei in the complex between DTBN and the Al^{3+} ions of various catalyst surfaces[6].

Constant	Al_2O_3	Type HY zeolite	$Al_2O_3 \cdot SiO_2$
$A_{\parallel}^{N}$	42.5	44.6	45.3
$A_{\parallel}^{Al}$	14.6	14.8	16.4
$A_{\perp}^{Al}$	11.2	12.5	14.2

Many workers now consider not only the difference in strength of the acidic centres on different catalysts but also the distribution in strength of the acidic centres (including acceptor centres) on any one catalyst[15]. In this case the

shift of the electron density from the donor (nitroxyl radical) towards the acceptor (Al^{3+} ion) should be different for different centres on the same surface. Therefore the observed ESR spectrum of the complex between the nitroxyl radical and the acceptor centre should be the sum of a number of spectra differing in the value of the constant for the HFI of the unpaired electron with the ^{14}N and ^{27}Al nuclei. In the models[6] of the spectra of the complex between the nitroxyl radical and the Al^{3+} ions on various catalyst surfaces no allowance was made for the distribution of the acceptor centres in acidic strength, i.e. each spectrum was characterised by a single value of the anisotropic HFI constant. By varying these constants the model spectra could be made to reproduce the experimental spectra satisfactorily. These values of the HFI constant are given in Table 2.

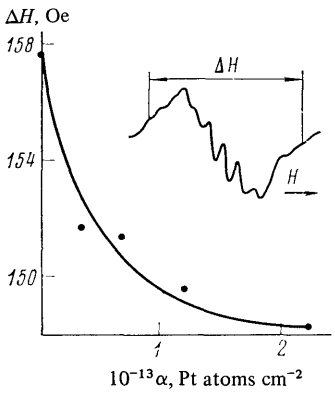


Figure 3. Variation of the parameter $\Delta H = 2A_{\parallel}^{N} + 5A_{\parallel}^{Al}$ for the ESR spectrum of adsorbed radical (I) with the concentration of platinum on a γ-Al_2O_3 surface.

We have recently shown† that the ESR spectra of the radical (I) complexed with coordinationally unsaturated Al^{3+} ions on a γ-Al_2O_3 surface is indeed the sum of a number of spectra for the radical (I) complexed with acceptor centres of different strength. Hence the parameter ΔH (defined[6] as $\Delta H = 2A_{\parallel}^{N} + 5A_{\parallel}^{Al}$) is an average quantity which can be used as a measure of the distribution in strength of the acceptor centres (Fig.3). We note that a change in acceptor strength causes a change in the same sense in both the constants $A_{\parallel}^{N}$ and $A_{\parallel}^{Al}$. We can therefore use the parameter ΔH to describe the effect of various factors (such as the surface activation or modification temperature) on the strength distribution of the acceptor centres.

For example, when platinum is deposited on a γ-Al_2O_3 surface the ΔH parameter decreases (Fig.3), showing that the distribution of acceptor centres has been shifted towards lower strengths (i.e. that the acceptor properties of the surface have been weakened by the metal–substrate interaction). Raising the activation temperature of the γ-Al_2O_3 increases the contribution from strong acceptor centres.

The adsorption of a small amount of the radical (I) on an activated γ-Al_2O_3 surface results in almost total complexing of the radical with the acceptor centres. This observation is consistent with the general belief that Al^{3+} ions are stronger than OH groups as adsorption centres for donor molecules. Similar results were obtained by Lozos and Hoffman[6] for the adsorption of DTBN at room temperature. Somewhat unexpectedly, these workers also observed a reversible migration of the DTBN from the acceptor centres to the OH groups when the temperature was lowered to −78 °C (indicated by the appearance of a triplet spectrum for the complex). Their estimate of the change in enthalpy accompanying the transfer of the radical from an OH group to an acceptor centre is approximately +5 kcal $mole^{-1}$. This result is explained in terms of the formation of a complex[16] between a coordinationally unsaturated Al^{3+} ion and a surface hydroxyl group. This requires the breaking of a bond between the OH group and the Al^{3+} ion in order to form a complex between the radical and the acceptor centre, with a corresponding expenditure of energy. However, an attempt to reproduce Lozos and Hoffman's experiment in our laboratory did not give the same result: no changes were observed in the ESR spectrum of activated alumina samples containing DTBN or the radical (I), even after lengthy storage at −78 °C, the spectrum at all times indicating complex formation with the Al^{3+} ions.

Non-polar adsorbates do not dissociate the complex between radical (I) and the acceptor centres: the characteristic spectrum is unchanged (Fig.2*a*) by the addition of an excess of toluene to the system. Polar adsorbates with donor properties (pyridine, n-butylamine, alcohols, water, ammonia) displace the radical (I) from the acceptor centres as shown by the appearance of a triplet spectrum[13,17,18].

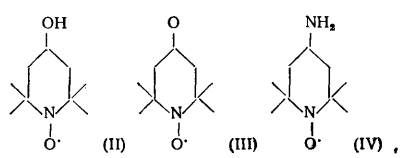
The displacement of the radical (I) from the acceptor centres begins at low coverages of the surface by donor adsorbates (10–30% of a monolayer)[18]. The molecules of (I) detached from the acceptor centres are held on OH groups, as shown by the change of the spectrum of the complex into a triplet spectrum with $A_{\parallel} \cong 38$ Oe.

The surface of fluorinated Al_2O_3 and of alumina–silicas contains acidic centres of two types: protonic and aprotic. The ESR spectrum of radical (I) adsorbed on these surfaces includes a contribution from the complex between the radical and the Al^{3+} ions[11]. Therefore, radical (I) is able to "discover" the acceptor centres irrespective of the protonic acidity of the catalyst. However, the ESR spectrum invariably contains a contribution from a triplet with $A_{\parallel} \cong 40$ Oe.[19] This large value of $A_{\parallel}$, almost identical to the $A_{\parallel}$ value in phosphoric acid (39.5 Oe), suggest complex formation between the >N–O· group of the radical and the protonic centres of the surface. This interpretation of the triplet with $A_{\parallel} = 40$ Oe is consistent with the observation that its contribution to the spectrum of the adsorbed radical (I) decreases when the protonic acidity of fluorinated Al_2O_3 is suppressed by exchange with Na^+ ions.

Thus radical (I) can be used for the qualitative detection of acidic centres of both the protonic and the aprotic (acceptor) type.

Donor pyridine molecules can displace radical (I) from both protonic and aprotic acidic centres, as shown by the decrease in the $A_{\parallel}$ constant of the triplet and the decreased spectral contribution from the complex produced by an increase in the coverage of the alumina–silica surface by pyridine[19].

By varying the structure of the nitroxyl radical we can model interactions of different adsorbates with the surface[7]. Thus, the radicals (II)–(IV) below contain, in addition to the N–O· group, a second donor group (oxy, oxo, and amino respectively):



†T.V.Bychkova, E.V.Lunina, A.K.Selivanovskii, and B.V.Strakhov, Zhur.Fiz.Khim. (in press).

In this case the two donor groups of a given molecule can compete for a specific adsorption centre. The spectrum of the complex between the N–Ȯ group and the Al^{3+} ions is not observed when the radicals (II)–(IV) are adsorbed on an activated Al_2O_3 surface. Hence we may conclude that the >N–Ȯ group is weaker as a donor than the oxy, oxo, or amino group. The parameter $A_{\parallel} = 36$ Oe suggests interactions between the paramagnetic group and the polar parts of the Al_2O_3 surface. Adsorption of the radicals (II)–(IV) on SiO_2, like their adsorption on Al_2O_3, results in bond formation between the specific adsorption centres (OH groups on the SiO_2 surface) and the second donor group (rather than the >N–Ȯ group), with $A_{\parallel} = 36.8$ Oe. This value of $A_{\parallel}$ indicates that the paramagnetic group is interacting with the polar elements of the SiO_2 surface.

Thus, for the "two-centre" molecules (II)–(IV) we must postulate a two-point adsorption model.

An excess of non-polar toluene molecules has no effect on the bond between the >N–Ȯ groups of the radicals (II)–(IV) and the SiO_2 or Al_2O_3 surface (as shown by the invariance of the $A_{\parallel}$ parameter). Pyridine breaks this bond, lowering $A_{\parallel}$ to 34.6 Oe at monolayer coverage[7].

The interaction of the nitroxyl radicals with specific adsorption centres can be detected also by observing the rotational mobility of these radicals on the surface[7]. It appears from these measurements that in order to displace from the specific adsorption centres the radicals (II)–(IV), which contain very strongly donating groups, we require higher concentrations of donor adsorbates than in the case of radical (I). Radical (IV) is more difficult to displace from the specific adsorption centres than radical (II): this reflects the more marked electron-donor properties of the amino group as compared to the oxy group.

It is clear from these results that the paramagnetic probe method can be used to monitor the distribution of typical donor molecules (the nitroxyl radicals) among adsorption centres of three types (hydroxyl groups, protonic acidic centres, and aprotic acidic centres), and to observe changes in this distribution caused by the adsorption of various substances.

III. INTERACTION OF DONOR MOLECULES WITH THE ACCEPTOR CENTRES OF γ-Al_2O_3

The displacement of radical (I) from acceptor centres by donor molecules (see above) can be used to investigate the interaction between these donor molecules and the acceptor centres[18]. After the adsorption of small amounts of donor molecules on an Al_2O_3 surface some of the acceptor centres remain free. The radical (I) (in amounts much smaller than the number of acceptor centres) is complexed with these free centres to give the ESR spectrum shown in Fig. 2*a*. If all the acceptor centres are blocked by molecules of the donor adsorbate the radical (I) has to compete with the donor adsorbate for the acceptor centres. Under these conditions some of the molecules of radical (I) are adsorbed on OH groups, and a triplet component appears# in the ESR spectrum of the adsorbed radical (I). Hence, by using the radical (I) as an indicator of free acceptor centres we can determine the amount of different donor molecules (bases) needed to fill the acceptor centres.

#The ESR spectra were recorded after lengthy (~5 days) storage of the sample at room temperature, to allow sufficient time for the redistribution of adsorbates over the adsorption centres to go to completion (see below).

It is clear from Table 3 that different surface concentrations are needed to fill all the acceptor centres of γ-Al_2O_3 with different bases. To account for this difference an independent study of each base is required, but one possible reason is the difference in selectivity of the bases with respect to the adsorption centres of the surface. Thus, pyridine is selectively adsorbed on the acceptor centres[20]. Water molecules can be strongly held by the OH groups, and have a tendency to associate on the surface[21]. The low effectiveness of alcohols in this respect is due, no doubt, to their chemisorption on OH groups with formation of alcoholates[22].

Table 3. Surface concentration of donor molecules (α) needed to fill the acceptor centres of γ-Al_2O_3 ($T_a = 470$ °C).[18]

Base	$10^{-13}\alpha$, cm^{-2}	θ*, % of monolayer
Pyridine	3±0.5	8
n-Butylamine	3±0.5	6
Ammonia	7±1	9
Isopropanol	7±1	20
n-Butanol	8±1	25
t-Butanol	7±1	22
Water	16±2	17

*θ is the degree of coverage of the surface.

The most interesting of the adsorbates which were examined is water, since it is a component of practically all catalytic systems, and the amount and form of the adsorbed water can have a profound effect on the activity of acidic heterogeneous catalysts. The number of water molecules needed to cover all the acceptor centres of γ-Al_2O_3 is $(16 \pm 2) \times 10^{13}$ cm^{-2} (see Table 3). This amount is independent of the adsorption temperature between 20 and 250 °C.[23] However, water adsorbed at 20 °C is removed from the surface much more easily than water which has been adsorbed at higher temperatures. Thus, in samples treated[23] with saturated water vapour at 20 °C for 2 days and then activated at 300 °C for 4 h in a vacuum of 10^{-5} Torr the concentration of acceptor centres§ was 2.0×10^{13} cm^{-2}. The acceptor properties of samples re-hydroxylated at a higher temperature (300 °C, 2 h, in an atmosphere of water vapour) and then activated under the same conditions (300 °C, 10^{-5} Torr, 4 h) were much less marked (0.8×10^{13} cm^{-2}).§ Evidently, the form of the adsorbed water varies with the adsorption temperature: molecular adsorption is predominant at low temperatures, and at higher temperatures the adsorption is mainly dissociative, with formation of OH groups, as indicated also by i.r. spectroscopic studies[24].

Ammonia is one of the probes most widely used in i.r. spectroscopy to analyse the acidic properties of the surface of oxide catalysts[8]. The amount of ammonia chemisorbed is taken as a measure of the concentration of acidic centres on the catalyst (in particular the aprotic centres of γ-Al_2O_3 [25]). However, the validity of this assumption requires justification: ammonia is known, from studies by i.r. spectroscopy[24], to interact not only with electron-acceptor centres (aprotic acids) but also with the surface oxygen ions of γ-Al_2O_3.

§The concentration of acceptor centres was determined by titration with pyridine, using the radical (I) as indicator[20].

The low selectivity of the adsorption of ammonia on the acceptor centres of γ-Al_2O_3 has been demonstrated also by the paramagnetic probe method[53]. 2.5×10^{13} cm^{-2} of pyridine was adsorbed on a γ-Al_2O_3 surface containing 3×10^{13} cm^{-2} of acceptor centres. 4.5×10^{13} cm^{-2} of ammonia was needed to fill the 0.5×10^{13} cm^{-2} acceptor centres which were still free. Hence, at least 4×10^{13} cm^{-2} of ammonia can be adsorbed on other centres.

We note that this amount (4×10^{13} cm^{-2}) does not change when the activation temperature of the γ-Al_2O_3 is raised to 700 °C, or when the catalyst is treated with hydrogen at high temperatures. A large volume of indirect information, as well as the results obtained by i.r. spectroscopy[24], suggests that in addition to the acceptor centres and oxygen ions on the surface of γ-Al_2O_3 can act as adsorption centres for ammonia.

IV. USE OF NITRIC OXIDE AS A PARAMAGNETIC PROBE

Many workers have used nitric oxide (NO) as a paramagnetic probe. Like the nitroxyl radicals, NO is an indicator of free acceptor centres on a catalyst. When adsorbed on these centres NO gives an ESR spectrum containing hyperfine structure from one ^{27}Al nucleus (Fig. 4*a*). However, in contrast to the radical (I), the ESR spectrum of NO can be observed only if the probe molecule is exposed to a fairly high electrostatic field gradient[27]. The NO molecules which are adsorbed on centres lacking in high crystal field gradient do not contribute to the ESR spectrum. This feature, together with the possibility of dimerisation of NO, is responsible for the low intensity of the ESR spectra of adsorbed nitric oxide, apparently uncorrelated with the number of adsorbed molecules[27-29] (unlike the ESR spectra of nitroxyl radicals). Another special feature of NO as a paramagnetic probe is that the NO molecules at room temperature are only weakly adsorbed on surfaces such as Al_2O_3, alumina–silicas, and zeolites. Substantial adsorption occurs only when the temperature is lowered to 77 K.

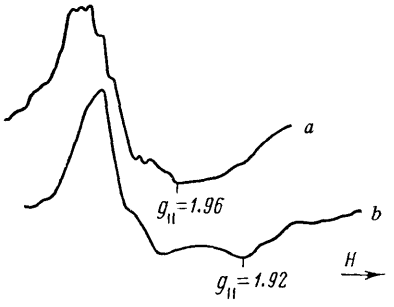


Figure 4. ESR spectra of nitric oxide adsorbed on γ-Al_2O_3 at −196 °C:[29] (*a*) adsorption on an activated γ-Al_2O_3 surface; (*b*) adsorption on a γ-Al_2O_3 surface containing 5×10^{13} cm^{-2} pyridine molecules.

This latter factor is extremely important, since in the quantitative determination of aprotic acidity by titration with bases (or in studies of the filling of acceptor centres) using nitroxyl radicals as indicators competition for the acceptor centre can occur between the titrant base (for example, pyridine) and the nitroxyl radical. This competition can distort the result of the determination. When NO is used as a probe its adsorption takes place at such low temperatures that the other adsorbed molecules are practically immobile. Therefore the competition is kinetically excluded (though it may be allowed thermodynamically). The concentrations of acceptor centres on γ-Al_2O_3 measured by pyridine titration using the radical (I) and NO as indicators [$(3.0 \pm 0.5) \times 10^{13}$ and $(4.0 \pm 0.5) \times 10^{13}$ cm^{-2} respectively] are in acceptable agreement[29]. This means that the competition between the base and the indicator does not play a major role when the number of acceptor centres is measured by the adsorption of pyridine using radical (I) as the indicator.

By using NO as the paramagnetic probe it was shown that 2,6-dimethylpyridine, like pyridine, is selectively adsorbed on the acceptor centres of a γ-Al_2O_3 surface. However, the presence of two methyl substituents makes the bond between the 2,6-dimethylpyridine molecules and the acceptor centres much weaker than in the adsorption of pyridine (steric hindrance).

When NO is adsorbed on a γ-Al_2O_3 surface two types of centre can be distinguished in the ESR spectra[26,29]. The first type are the centres containing coordinationally unsaturated Al^{3+} ions: they give an ESR spectrum with HFS from the Al nucleus. Centres of the second type also have a large crystal field gradient, but their ESR spectrum does not contain HFS from the Al nucleus (Fig. 4*b*).

It is interesting to note that in the adsorption of pyridine the centres of the first type are filled first[29]. As long as the concentration of pyridine does not exceed 3×10^{13} cm^{-2}, centres of the first type remain free on the Al_2O_3 surface. NO is adsorbed on these centre giving the ESR spectrum shown in Fig. 4*a*. A pyridine concentration of 4×10^{13} cm^{-2} is sufficient to block all the centres of the first type. In this case the NO is adsorbed on centres of the second type, and gives the ESR spectrum shown in Fig. 4*b*. Thus, in the first instance both pyridine and NO are adsorbed on centres of the first type, leaving the second type of centre free. A similar behaviour is observed with 2,6-dimethylpyridine.

When ammonia is adsorbed, centres of the first type are observed in the ESR spectra of NO until the concentration of ammonia reaches 8×10^{13} cm^{-2}. At still higher concentrations of ammonia the ESR spectrum of NO cannot be detected. Hence, the ammonia molecules (unlike pyridine) can fill centres of both types, the probability of filling centres of the second type being equal to (or greater than) the probability of filling centres of the first type (coordinationally unsaturated Al^{3+} ions).

V. DETERMINATION OF THE CONCENTRATION OF ACCEPTOR CENTRES IN γ-Al_2O_3

When a small amount of the nitroxyl radical (I) is adsorbed on an activated γ-Al_2O_3 surface all the adsorbed molecules are bound to surface acceptor centres (only the spectrum shown in Fig. 2*a* is observed[30]). Hence, this radical is selectively adsorbed on the acceptor centres. Assuming that the OH groups are much weaker adsorption centres than the acceptor centres we can expect the acceptor centres to be filled first, followed by the OH groups, as the concentration of the radical on the surface is increased. This idealised behaviour is illustrated by the broken lines in Fig. 5. The experimental curves (full lines) are not very different, though they show a marked smoothing of the sharp breaks (Fig. 5). Since the surface complex consists of one molecule of radical (I) and one acceptor centre the number of acceptor centres in the sample can be identified with the maximum amount of radical (I) bound in the complex.

The high sensitivity of ESR allows small concentrations of acceptor centres to be determined (as in γ-Al_2O_3 samples activated at low temperatures). For example, on γ-Al_2O_3 activated in a vacuum at 150 °C a concentration of ~10^{11} cm^{-2} has been observed[30]. When the vacuum heat treatment temperature was raised to 200 °C the concentration of acceptor centres rose to 4×10^{12} cm^{-2}.[30]

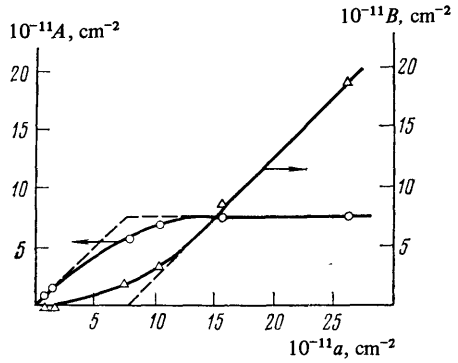


Figure 5. Dependence of the concentration of radical (I) complexed with Al^{3+} ions (*A*) and of the concentration of radical (I) not complexes with Al^{3+} ions (*B*) on the total concentration of radical (I) adsorbed on a γ-Al_2O_3 surface (*a*) activated in air at 300 °C.[30] The broken lines show the idealised dependence.

As the vacuum activation temperature is further increased the concentration of acceptor centres increases still further. The determination of these large concentrations requires the addition of large amounts of radicals. This introduces a difficulty, inherent in ESR: the dipole–dipole interaction causes broadening of the HFS of the spectrum when the radicals are closely spaced on the surface, and the spectrum is converted into a broad, structureless line. In such a spectrum it is very difficult to resolve the contribution from the spectrum of Fig. 2*a*, i.e. to determine the amount of radical (I) bound in the complex, and hence the number of acceptor centres[30]. In this case another approach can be followed: titration of the acceptor centres with an organic base (pyridine) using radical (I) as the indicator[20]. The choice of pyridine is dictated by the outstanding effectiveness of this molecule in filling the acceptor centres (see Table 3). The surface concentration of pyridine for which the filling of the acceptor centres is complete is taken as a measure of the concentration of acceptor centres. The acceptor properties of γ-Al_2O_3 activated at widely different temperatures were determined by this method: the results are summarised in Fig. 6.

However, the titration method is, to some extent, indeterminate, since the titrant base can be adsorbed also on adsorption centres other than the acceptors. The validity of the results can be estimated by analysing a similar series of samples by an independent method[20]: from the concentration of the paramagnetic donor–acceptor complex formed by anthraquinone[31]. The results are shown in Fig. 6, together with the concentrations of acceptor centres in γ-Al_2O_3 samples activated at low temperatures[31]. These values were obtained by a direct method, i.e. as the maximum concentrations of the complexed form of radical (I) (see above). As Fig. 6 shows, the agreement between the three independent methods is good. We may therefore suggest that all the acceptor centres detected by these methods are the same: coordinationally unsaturated Al^{3+} ions. In this sense the work is very different from previous publications[15,32], in which the numerical results were highly tentative.

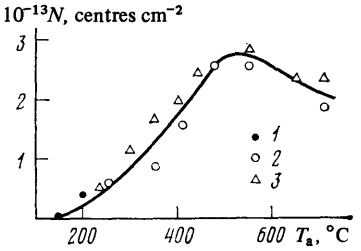


Figure 6. Dependence of the concentration of acceptor centres on γ-Al_2O_3 on the activation temperature of the catalyst[20]. Concentrations determined: *1*) as the limiting concentration of complexed radical, *2*) by titration with pyridine using the radical (I) as indicator, *3*) from the concentration of the paramagnetic donor–acceptor complex with anthraquinone.

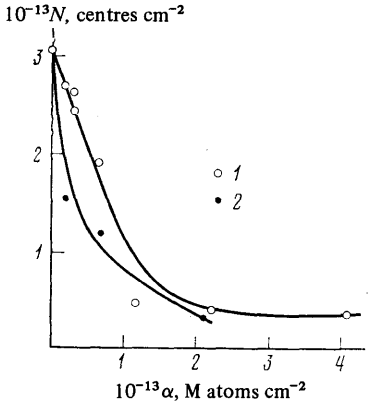


Figure 7. Concentration of acceptor centres on the surface of alumina–platinum and alumina–palladium catalysts against concentration of metal M: *1*) platinum, *2*) palladium.

Pyridine titration with radical (I) as indicator was used to measure the concentration of acceptor centres on alumina–platinum and alumina–palladium catalysts¶. We see from the results (Fig. 7) that the introduction of the metal lowers the concentration of acceptor centres very significantly, especially in the range $0.2–1.0 \times 10^{13}$ metal atoms cm^{-2}. The decrease in the concentration of acceptor centres is due to the interaction of the deposited metals with the γ-Al_2O_3 surface. The effect of the metals on the acceptor properties of the γ-Al_2O_3 is very strong. Thus, even assuming that the

¶T.V.Bychkova, E.V.Lunina, A.K.Selivanovskii, E.A.Nikel', T.Yu.Samgina, and B.V.Strakhov, Zhur.Fiz. Khim. (in press).

whole of the metal is in an atomic state and evenly distributed over the acceptor states (i.e. on the most favourable assumption) each metal atom has to block two acceptor centres at a metal concentration of 1×10^{13} atoms cm^{-2}. However, in real systems the deposited metals are known to be present as microcrystals. Therefore, the effectiveness of the suppression of surface acceptor centres by metal atoms is even greater than the above estimate. For example, in a sample containing 1.7 wt.% of platinum a single crystallite (average diameter 10 Å) can suppress the acceptor properties over an area 100 times greater than its own area, i.e. such a crystallite exhibits long-range effects. As has already been pointed out, the strength of the remaining acceptor centres also decreases very markedly.

Thus the application of the paramagnetic probe method in the study of bifunctional catalysts (Pt/Al_2O_3 and Pd/Al_2O_3) can yield technologically useful information on the interactions between the metal and the support.

On surfaces containing proton-donor centres as well as acceptor centres (for example, fluorinated Al_2O_3, alumina–silicas, decationated zeolites[11,19,38]) the radical (I) is unstable, and the concentration of acceptor centres is difficult to determine. The difficulty can be avoided by lowering the proton acidity (i.e. by exchanging the protons with alkali metal ions). This treatment stabilises the adsorbed radical (I) [19,33] without affecting the concentration of the acceptor centres, at least when the concentration of alkali metal ions is small[33].

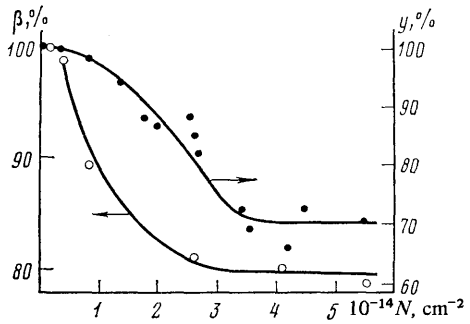


Figure 8. Dependence of the catalytic activity and of the acceptor capacity of γ-Al_2O_3 on the amount of cyclohexanol dehydrated on the catalyst surface at 150 °C: [34] y is the extent of conversion of the cyclohexanol, β is the acceptor capacity of the catalyst at the end of the experiment in arbitrary units (i.e. the contribution of the complex between radical (I) and the Al^{3+} ions to the overall ESR spectrum of the adsorbed radical (I).

VI. STUDY OF CATALYTIC PROCESSES

A very interesting possibility of the paramagnetic probe method is the study of the surface state of a catalyst during or immediately after the catalytic process. The radical (I) has been used[18,34] to indicate changes in the acceptor strength of a catalyst during the dehydration of an alcohol. Dehydration of isopropanol, n-butanol, and *t*-butanol was carried out in the adsorption layer of γ-Al_2O_3 at 100 °C.[18] The amount of alcohol adsorbed was sufficient to fill all the acceptor centres, with a slight excess. As a result of the dehydration reaction some of the acceptor centres were set free: the radicals (I) present on the surface were able to combine with these centres to form a complex. The freeing of the centres is due to the fact that the resulting alkenes are transferred to the gas phase, and water is less effective than alcohols in filling acceptor centres (see Table 3). All the acceptor centres are occupied when the amount of pre-adsorbed alcohol (and therefore the amount of water produced) is $(15 \pm 2) \times 10^{13}$ cm^{-2}. This value is almost the same as the concentration of water molecules needed to fill all the acceptor centres.

Thus, during the dehydration of alcohols the acceptor capacity of γ-Al_2O_3 is determined mainly by the concentration of water on the surface. This problem has been studied in detail[34], using as an example the dehydration of cyclohexanol on γ-Al_2O_3, and it was shown that a stationary catalytic activity and a stationary concentration of acceptor centres are set up during the catalytic experiment, depending only on temperature (Fig. 8). Evidently, the water produced by the dehydration reaction is partially desorbed from the surface, resulting in a steady state in which a definite concentration of catalytically active centres (Al^{3+} ions) remains invariant. As the temperature of the catalytic experiment decreases the desorption of water becomes more sluggish, lowering both the concentration of free acceptor centres and the catalytic activity of the sample.

The catalytic hydrogenation of di-*t*-butylnitroxyl on platinised silica gel and alumina surfaces has been studied[35] at −70 °C. The reaction product was the corresponding hydroxylamine:

$$(CH_3)_3C\diagdown\!\!\diagup N\!-\!\dot{O} + {}^1/_2 H_2 \rightarrow (CH_3)_3C\diagdown\!\!\diagup N\!-\!OH\ .$$
$$(CH_3)_3C \qquad\qquad (CH_3)_3C$$

The progress of the reaction was monitored by ESR from the decrease in the concentration of radicals. Most of the results were obtained on SiO_2 (specific surface area $S = 340$ m^2 g^{-1}) containing 1.2% of Pt. The platinum was shown to be present as microcrystals containing an average of 5400 atoms. Therefore the average distance between Pt crystals on the surface was greater than 1000 Å. (Note that a distance of 100 Å is erroneously quoted in the original paper[35]). The coverage of the surface by the radical was fairly high ($\theta \cong 0.25$). Thus the distance between platinum crystals was almost two orders of magnitude greater than the distance between radicals. Therefore we could have expected the dehydration to be confined to those molecules in the immediate vicinity of Pt crystals, keeping the distance between the unreacted molecules constant. However, the ESR spectral changes during the hydrogenation (at −70 °C) indicate a uniform decrease in the concentration of the radical over the entire surface, i.e. an increase in the average distance between radicals. This observation implies a fairly high mobility of the particles in the adsorption layer, even at −70 °C. However, the mobile adsorbate (the radical, or an active form of hydrogen) has not yet been identified.

Nitroxyl radicals, though usually added to catalytic systems as probes or as reactants, can be generated on the surface by certain processes. The simplest is the oxidation of the corresponding hydroxylamine. It has been shown[35] that the hydroxylamine produced by reducing di-*t*-butylnitroxyl adsorbed on platinised silica gel or Al_2O_3 can be oxidised back to the initial radical by oxygen at 25 °C. Under these conditions the concentration of the resulting nitroxyl is not more than 27% of the concentration of the initial radical. Surprisingly, the nitroxyl prepared by oxidising a hydroxylamine on platinised Al_2O_3 is adsorbed on hydroxyl groups rather than on Al^{3+} ions. Apparently the Al^{3+} ions, having interacted with the initial radicals, are blocked by the water molecules produced by the oxidation.

Another, more interesting, and far more usual case is the formation of nitroxyl radicals from nitroso compounds and nitrones by free radical capture. In this way the short-lived radicals formed as intermediates by various reactions can be exploited. The method, which so far has been applied mainly in studies of homogeneous systems[36-38], has been called the spin trap method. In principle this method should give interesting information on reactions in heterogeneous systems.

The interation of *t*-nitrosobutane (TNB) with the activated surface of various oxides has been studied in our laboratory[39,40]. In these experiments the TNB was, simultaneously a reactant undergoing free-radical decomposition and a spin trap:

$$(CH_3)_3C{-}NO \xrightarrow{cat.} (CH_3)_3C^{\cdot} + NO$$
$$(CH_3)_3C^{\cdot} + (CH_3)_3C{-}NO \rightarrow (CH_3)_3C{-}\underset{\underset{O^{\cdot}}{|}}{N}{-}C(CH_3)_3 .$$

The experiments were carried out at room temperature in the dark in order to eliminate the side-reaction (decomposition of the TNB under the influence of light). The nitroxyl radicals produced by the above reaction can easily capture alkyl radicals with formation of diamagnetic adducts:

$$(CH_3)_3C^{\cdot} + (CH_3)_3C{-}\underset{\underset{O^{\cdot}}{|}}{N}{-}C(CH_3)_3 \rightarrow (CH_3)_3{-}\underset{\underset{C(CH_3)_3}{|}}{\overset{\overset{O}{|}}{N}}{-}C(CH_3)_3 ,$$

Therefore the activity of the catalysts towards the radical decomposition of TNB was estimated from the initial portion of the kinetic curve describing the formation of nitroxyl radicals, in which the latter reaction can be ignored.

Catalytic free-radical decomposition of TNB is observed on the surface of many oxides: MgO, ZnO, γ-Al_2O_3, Ga_2O_3, Y_2O_3, Sc_2O_3, La_2O_3, and SiO_2. It was shown[39,40] that the reaction occurs most readily on the surface of oxides having semiconductor properties, less readily on γ-Al_2O_3, and is almost undetectable on silica gel. These observations led to the hypothesis that the electron-donor centres on the surface are responsible for the radical decomposition process. The structure of the trapped butyl radical depends on the nature of the surface: on all the oxides except Al_2O_3 and Sc_2O_3 it is the normal *t*-butyl radical, formed by the decomposition of TNB. On γ-Al_2O_3 and Sc_2O_3 surfaces the *t*-butyl radical undergoes isomerisation to isobutyl, but the mechanism of this process has not yet been studied in detail.

The nitroxyl radicals formed by the radical decomposition of TNB also act as paramagnetic probes, and thus allow us to characterise the state of the surface. For example, the ESR spectra of these radicals formed on the surface of γ-Al_2O_3, Ga_2O_3, Sc_2O_3, and La_2O_3 include additional HFS from the nuclei ^{27}Al ($I_{Al} = 5/2$), $^{69,71}Ga$ ($I_{Ga} = 3/2$), ^{45}Sc, and ^{139}La ($I = 7/2$) respectively, i.e. the formation of donor–acceptor complexes is observed. Whereas on γ-Al_2O_3 and Ga_2O_3 these complexes can be produced by the adsorption of synthetic di-*t*-butylnitroxyl, this could not be done with Sc_2O_3 and La_2O_3. A probable explanation is that the Sc^{3+} and La^{3+} surface cations are available for the adsorption of nitroxyl radicals only during the catalytic decomposition of TNB.

These results highlight the importance of the spin trap method in studies of the mechanism of catalytic reactions and of the surface structure of working catalysts.

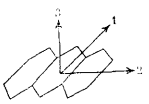
VII. STUDY OF THE DYNAMICS OF THE ADSORPTION LAYER

Information on the dynamics of the adsorption layer is highly relevant to an understanding of adsorption and catalytic processes. For example, if the surface mobility of the reactants is limited the effective rate constant of heterogeneous catalytic reactions is found[41] to be a function of the surface diffusion coefficient (i.e. of the velocity of translational motion). The velocity of rotation of the adsorbed molecules should also affect the rate of bimolecular catalytic reactions. For bimolecular reactions in rigid polymeric matrices this correlation between the rates of reaction and of molecular rotation has been established[42-44]. In the case of the bimolecular disproportionation of nitroxyl radicals adsorbed on alumina–silica the rate of the catalytic process was found to be determined by the mobility of the adsorbed molecules[19].

Studies of the mobility of adsorbed molecules are experimentally difficult, but significant advances have been made by the application of radio-frequency spectroscopy methods (and especially ESR).

The intensity of the rotational motion of the molecules is traditionally characterised by the correlation time $\tau_C = 1/\nu$, where ν is the rotation frequency[4]. By modelling the experimental spectra on a computer the correlation times describing the rotational mobility of the adsorbed molecules can be evaluated. This type of analysis of the ESR spectra of the cation radicals of polycyclic hydrocarbons adsorbed on alumina–silica[45] has shown that the rotation rates are quite high and the rotation is almost axially symmetrical (Table 4).

Table 4. Correlation times for the rotation of polycyclic hydrocarbon cation radicals adsorbed on alumina–silica[45].



Adsorbate	$10^{10}\tau_C$, s		
	τ_{C_1}	τ_{C_2}	τ_{C_3}
Perylene	27.5	3.9	2.75
Anthracene	21	2.1	2.1
Tetracene	42	3.5	2.8

Table 5. Correlation times τ_C for the rotation of radical (I) adsorbed from the vapour on SiO_2 at 20 °C.[23]

Adsorbent	S, $m^2 g^{-1}$	Pore radius, A	$10^9\tau_C$, s	
			$T_a = 170$° C	$T_a = 470$° C
Silica gel	660	15; 35	7.0	7.0
Silica gel	365	45	6.2	6.2
Silica gel	200	93	6.8	6.8
Aerosil	130	—	6.0	6.2

Advances in our understanding of the shape of the ESR spectra of nitroxyl radicals have led to the development of simple procedures for calculating the correlation times for rotation over the whole range of characteristic times accessible to the ESR method: $10^{-11} < \tau_C < 10^{-7}$ s.[3,4] The correlation time for rotation in non-viscous solutions is less than 10^{-11} s. Adsorption on SiO_2 surfaces strongly inhibits the rotation of nitroxyl radicals (as compared with a solution)[6,46]. The rotational mobility of the radical (I) is practically independent of both the structural characteristics of the SiO_2 surface and the vacuum activation temperature of the adsorbent in the range 150–800 °C [23] (see Table 5). Throughtout this review the anisotropy of the rotation of adsorbed nitroxyl radicals will be ignored.

The HFS components of the ESR spectra of radical (I) for samples activated at lower temperatures were found to be significantly broader than those of high-temperature samples[23]. Line broadening in low-temperature samples is probably due to the fact that the observed spectrum is a sum of spectra corresponding to different values of τ_c. This may be a consequence of the presence of different types of adsorption centre. The narrowing of the spectrum in SiO_2 samples activated at high temperatures suggests greater uniformity of the adsorption centres after high-temperature treatment.

The distribution of correlation times for the rotation of di-*t*-butylnitroxyl adsorbed on SiO_2 is clearly demonstrated in Ref.47. At low microwave powers (i.e. far from saturation) the contribution from slowly rotating molecules is predominant in the ESR spectra. At higher microwave power levels (under conditions of saturation) the major contribution comes from rapidly rotating molecules, whose rate of rotation is approximately 5 times greater. The presence of radicals differing in rate of rotation by more than 4 orders of magnitude on the SiO_2 surface (from $\tau_c > 10^{-5}$ to $\tau_c \cong 3 \times 10^{-9}$ s) has been demonstrated by the fast adiabatic pass method.

The activation energy for the rotation of the radical (I) on the surface of SiO_2 is ~2 kcal mole^{-1}.[46] A similar value (1.9 kcal mole^{-1}) is obtained for di-*t*-butylnitroxyl[6]. Allowing for the distribution of the correlation times of di-*t*-butylnitroxyl molecules Mailer and Hoffman[47] quote a value of 1.5 kcal mole^{-1} for the activation energy of rotation of the rapidly rotating molecules.

A non-polar solvent (toluene) increases the rotational mobility of the adsorbed radical (I), τ_c decreasing from 7.0×10^{-9} to 2.5×10^{-9} s.[46] This effect probably stems from a decrease in the non-specific interaction between the hydrophobic part of radical (I) and the surface.

a single value of τ_c is observed, also decreasing with increase of θ.

Sistovaris and coworkers[9] have studied the rotational mobility of different nitroxyl radicals adsorbed and "stitched" to the surface of SiO_2 samples which had been modified by "grafting" to the OH groups fragments such as $-(CH_2)_n-X$ (where X = H or NH_2, and $n = 2-8$). As the length of the hydrocarbon chain separating the paramagnetic $>\dot{N}-O$ fragment from the adsorption centre was increased the activation energy for rotation decreased from 8–10 to 2–5 kcal mole^{-1}. Non-polar solvents have almost no effect on the rate of rotation of the tracer (the paramagnetic fragment). Addition of a polar solvent increases the rotational mobility. The effect is most marked when the coverage of the surface by the polar solvent is a maximum.

Fox and coworkers[49] have used the paramagnetic probe method to study the adsorption of polymers from solution on SiO_2. From the ESR spectra of polymers labelled with nitroxyl radicals they were able to estimate the fractional number of segments actually adsorbed on the solid surface. Two values of the correlation time of the nitroxyl label are observed in the ESR spectra of these systems: a longer one, corresponding to slow rotation of the labels attached to segments of the polymer chain fixed to the surface, and a shorter one, corresponding to the faster motion of the chain fragments not bound to the surface.

When nitroxyl radicals are adsorbed on γ-Al_2O_3 or alumina–silica surfaces they form a complex with the Al^{3+} ions (as we have already pointed out) whose ESR spectrum is shown in Fig.2*a*. Lozos and Hoffman[6] estimate that the τ_c value for the rotation of di-*t*-butylnitroxyl in this case is close to the value for SiO_2 samples (6×10^{-9} s), with an activation energy for rotation of 1 kcal mole^{-1} (i.e. one-half the value for SiO_2).

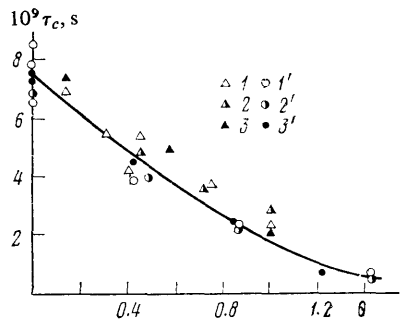


Figure 9. Mean correlation time (τ_c) for the rotation of radical (I) adsorbed on SiO_2 against coverage of the surface by adsorbed donor molecules (θ), from Ref.48: *1–3* adsorption of water, *1′–3′* adsorption of pyridine. Activation temperature of the SiO_2: 150 °C (*1* and *1′*), 300 °C (*2* and *2′*), 470 °C (*3* and *3′*).

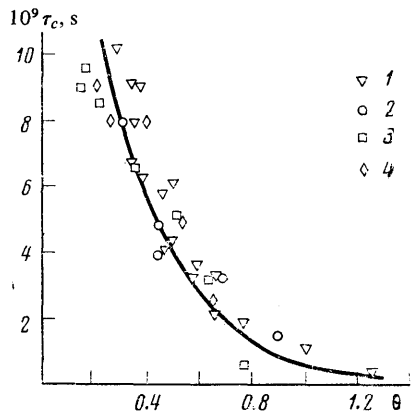


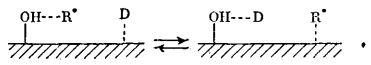
Figure 10. Mean correlation time (τ_c) for the rotation of radical (I) adsorbed on γ-Al_2O_3 ($T_a = 470$ °C) against coverage of the surface by adsorbed donor molecules (θ), from Ref.48. Adsorption: *1*) water, *2*) pyridine, *3*) n-butylamine, *4*) ammonia.

As we have already pointed out, donor adsorbates can displace the radical (I) from the surface OH groups. At surface coverages by donor molecules of $\theta \leq 0.7$ the rotational correlation times fall into two groups[48], corresponding to slow rotation of the specifically adsorbed radicals and fast rotation of the physisorbed radicals. As θ increases the proportion of physisorbed radicals increases, and the average value of τ_c correspondingly decreases (Fig.9). When $\theta > 0.7$

As in the case of the SiO_2 adsorbent, the rotational mobility of radical (I) adsorbed on activated γ-Al_2O_3 increases in the presence of a non-polar solvent (toluene)[14]. When donor molecules are adsorbed, radical (I) is displaced from the specific adsorption centres (first from the acceptor centres,

and then from the OH groups)[48]. At surface coverages of $0.3 \leq \theta \leq 1$ (as in the case of SiO_2) two forms of adsorption are observed: specific (on OH groups) and physical. Different values of τ_c apply to these forms. As θ increases the mean value of τ_c decreases because of the increased contribution from the rapidly rotating physisorbed molecules (Fig.10), and when $\theta > 1$ only one value of τ_c is observed.

These observations (the presence of one or two values of τ_c, or more probably of one or two groups of values of τ_c) can be explained by postulating an exchange between the adsorbate molecules:



In this scheme R· is a radical and D is a molecule of donor adsorbate. If this exchange is quite fast the system will have a single mean value of τ_c for rotation. The rate of exchange can be decreased by lowering the temperature of the sample. Under these conditions the ESR spectra yield two values of τ_c.[48] The situation is reversible: on raising the temperature the ESR spectrum can again be characterised by a single value of τ_c.

Thus, at the higher temperatures the life time of a molecule on an adsorption centre and the correlation time for rotation become comparable. Under these conditions it is meaningless to specify only rotational or only translational motion of the molecules, and it is more rational to consider a single rotational–translational motion. On the other hand if the molecule has a fairly long settled life time in its adsorption centre, and only seldom "jumps" from centre to centre, the two motions (rotational, and translational) can be considered separately.

ESR spectra are sensitive to the distance between the paramagnetic particles. From the dipole–dipole broadening of the spectra the average distance between nitroxyl radicals is found to be between 10 and 60 Å.[50] The time dependence of the average distance between adsorbed radicals has been used to characterise the translational mobility of the radicals.

An analysis[51] of the spectra of radical (I) adsorbed on SiO_2 has shown that the adsorption is initially very non-uniform, the distance between the nearest radicals being much smaller than the average distance. As a result of surface diffusion at room temperature these distances increase. The rate of surface diffusion is practically independent of the porosity and specific surface area of the silica gel sample. On raising the activation temperature of the sorbent the rate of increase diffusion decreases sharply. An estimate of the translational diffusion coefficients of radical (I) adsorbed on SiO_2 by the Einstein–Smoluchowsky equation gave value 12–15 orders of magnitude lower than in non-viscous liquids (10^{-20}–10^{-17} $cm^2\ s^{-1}$)[23].

In the presence of donor molecules (water, pyridine, alcohols, etc.) the translational mobility of radical (I) on a SiO_2 surface is sharply increased[48]. At a coverage by donor molecules of $\theta \cong 0.8$, and a mean distance between the radicals (I) of about 40 Å, the frequency of mutual collisions between the radicals becomes so high that exchange interaction becomes noticeable in the spectrum, as in the case of solutions in non-viscous solvents. Under these conditions the mobility of the molecules in the adsorption layer is comparable to the mobility of molecules in solution.

Because of the presence of acceptor centres the specific adsorption properties of γ-Al_2O_3 are much more marked than those of SiO_2. The radical (I) is adsorbed very non-uniformly on an activated γ-Al_2O_3 surface[52]. Localised concentrations of the radical (I) tend to disappear by surface diffusion, but whereas on SiO_2 this process is completed in a few hours at room temperature, on γ-Al_2O_3 it is still in progress after several days. The activation energy for surface diffusion is 29 ± 6 kcal $mole^{-1}$.[23] This value is close to the energy of the bond between the $\geq N-\dot{O}$ group and the acceptor centre, because this bond has to be broken when the radical (I) "jumps" from centre to centre.

The translational mobility of radical (I) adsorbed on γ-Al_2O_3 is increased (as in the case of the SiO_2 adsorbent) by the addition of donor molecules to the system[18,52]. The donor molecules displace the radical (I) from the acceptor centres, and a triplet component corresponding to radicals which are adsorbed but not complexed with Al^{3+} ions appears in the ESR spectrum as soon as a small addition of donor vapour is made to the system. Surface migration enables these radicals to form new complexes with the acceptor centres which are still free, and a spectrum similar to that shown in Fig.2*a* is gradually re-established. As a result the radical (I) becomes more evenly distributed over the surface. The relatively fast changes in the system come to an end when the radicals have become attached to the acceptor centres.

If the concentration of donor molecules is increased all the acceptor centres are occupied and some of the radicals (I) are unable to form complexes with the Al^{3+} ions: under these conditions a stable triplet appears in the ESR spectrum. The relative amounts of radical (I) which are (respectively) complexed or displaced from the acceptor centres are independent of the order in which the radical and the donor molecules were added to the system. They are determined only by the amount and the nature of the donor adsorbate, i.e. an equilibrium distribution of radical (I) and of the second donor adsorbate is gradually established over the adsorption centres of the γ-Al_2O_3.

The mobility of molecules of bases on the γ-Al_2O_3 surface can be studied by using NO as an indicator of free acceptor centres[29]. After the adsorption of 7×10^{13} cm^{-2} molecules of pyridine (i.e. almost double the amount needed to fill all the acceptor centres) a large number of free acceptor centres is observed during the first few hours in the ESR spectra of NO. Therefore the adsorption of pyridine is very non-uniform, with a large proportion of the adsorbate molecules on the outer surface of the adsorbent grains, leaving the internal surfaces free. Redistribution of the adsorbate over the surface takes place gradually, and after several days all the acceptor centres are occupied by pyridine molecules.

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Thus the paramagnetic probe method is likely to find increasing application in studies of adsorption and catalysis. It gives clear indications of the formation of an adsorption layer, and of its dynamics, and it can be used to characterise the interaction between adsorbed molecules and the active centres of the surface, i.e. to solve the fundamental problems in the physical chemistry of heterogeneous catalysis.

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