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An ESR Study of NO_2 Adsorbed on Silica Gel Surfaces[1]

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NO_2 adsorbed on silica-gel surfaces shows temperature-dependent ESR spectra, which can be explained by assuming a restricted rotation of the NO_2 molecule, where the preferred axis is the O–O direction. It is concluded from this observation that a hydrogen-bond force between the oxygen of NO_2 and OH groups on the silica-gel surfaces plays a part in the NO_2-silica-gel interaction. It is also estimated, from the observed hyperfine tensor, that the ONO angle may become slightly smaller when NO_2 is adsorbed onto the silica-gel surface from the gas phase.

It is considered that the adsorption of radicals on solid surfaces changes the nature of their motion from that in the gas phase, in solution, or in solid matrices. In many cases of studies of free radicals in adsorbed states, a restricted motion of the molecules has been detected through line-width-broadening effects in the ESR spectra.[2] However, there have been few cases where detailed information about the motion of the radicals or about the nature of the radical-surface interaction has been obtained.

In the present work we examined NO_2 adsorbed on the silica-gel surface by ESR with the aim of getting information about the adsorbed state. We found that NO_2 shows temperature-dependent ESR spectra, which can be explained by the restricted rotation of the molecule, where the preferred axis is the O–O direction. On the basis of this observation, it can be estimated that the NO_2 molecule interacts with the silica-gel surface through a hydrogen bond with OH groups on the silica-gel surface. The change in the molecular structure by adsorption is not large. However it is estimated that the ONO angle may become smaller when NO_2 is adsorbed on the silica-gel surface from the gas phase.

Experimental

The samples for ESR measurements were prepared by letting NO_2 gas be adsorbed on silica-gel surfaces in a vacuum line. The NO_2 used was obtained commercially (The Matheson Co., Inc.) and was dried with P_2O_5. Prior to treatment with NO_2, the silica gel (a Kanto Chemical Co. product for chromatography, 60—80 mesh) was heated for 6 hr at 500—550°C and at 10^{-6} Torr. The silica gel was then exposed to NO_2 gas at about 1 atm at room temperature. After exposing the silica gel to NO_2 for a few minutes, the excess NO_2 was removed by leading the gas into a trap cooled by liquid nitrogen. The ESR spectra were measured by a Hitachi model MES 4001 X-band ESR spectrometer at various temperatures ranging from room temperature to 77°K. The sample was cooled with a gas-flow cooler or with a liquid nitrogen dewar with an unsilvered lower section. The temperature of the sample was monitored by a copper-constantan thermocouple placed just below the sample tube in the cavity.

Results and Discussion

Hindered Rotation of NO_2 on Silica Gel. Figure 1 shows the ESR spectra of NO_2 adsorbed on the silica-gel surface at various temperatures. As Fig. 1 shows, the spectra are temperature dependent. The changes in the spectra were completely reversible upon changes in the temperature. The ESR spectra of NO_2 trapped in various solid matrices have been reported by a number of authors,[3-10] and it has been shown that they can be interpreted in terms of anisotropic hyperfine interaction with the nitrogen nucleus and anisotropic g factors, with the principal axes parallel to the molecular axes. In most of the cases treated in the solid matrices, the hyperfine and g tensors are unsymmetrical, as is to be expected from the molecular geometry. In the present case, however, the ESR spectrum observed at 77°K is interpreted by g and hyperfine tensors which are approximately axially symmetric. This indicates that the radical is rotating about this symmetry axis sufficiently rapidly to give a rotational average about the axis at this temperature. The experimental parameters obtained here are compared in Table 1 with those found in solid matrices. It may be seen from the table that the axis of the rotation is the y axis, *i.e.*, the O–O direction, and that the parameters of the x and z axes are averaged by the rapid rotation of the molecule. As the temperature increases, the absorption peak associated with the y axis disappears and the spectrum tends to become a triplet splitting with equal intensities, indicating that the rotation around the x and z axes becomes important.

According to theoretical calculations of the electro-

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[1] Presented at the symposium of ESR, Tokyo, October, 1970.

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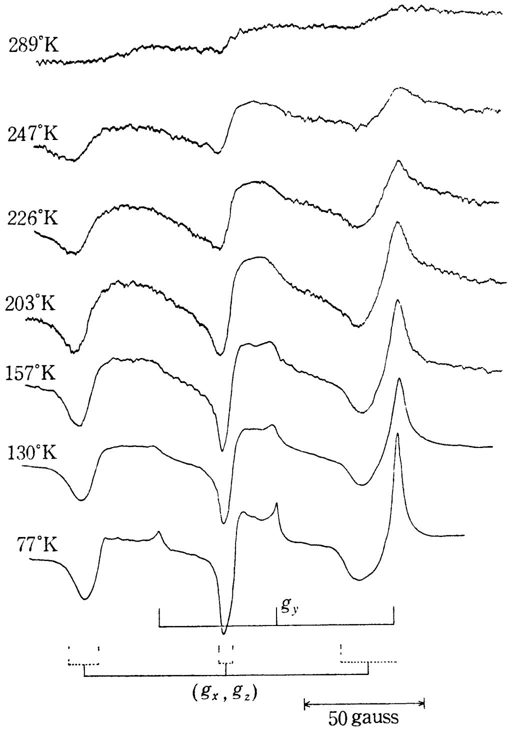

Fig. 1. ESR spectra of NO_2 adsorbed on the silica-gel surface at various temperatures.
Field increases from left to right.

nic structure of the NO_2 molecule,[13–17] it can be considered that a large net negative charge exists in the two oxygen atoms in the molecule. In view of the fact that NO_2 prefers to rotate about the O–O direction on the silica-gel surface, it is reasonable to consider that a hydrogen bond formed between the oxygen of the NO_2 molecule and OH groups on the silica-gel surface may play an important role in the interaction

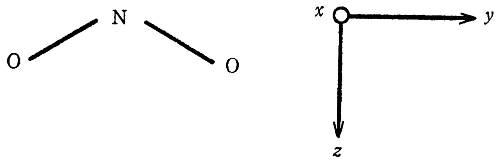

Fig. 2. Coordinate system for NO_2.

of the NO_2 molecule and the silica-gel surface. This model permits the rotation of the NO_2 molecule around the O–O direction. Previously Rozenberg *et al.*[18] pointed out, on the basis of experiments on the adsorption capacity of the silica gel as a function of the dehydration temperature, that the hydrogen-bond force may participate in the adsorption of NO_2 on the silica-gel surface. Our conclusion from the ESR experiments agrees with their result.

Recently, a study of NO_2 adsorbed in synthetic zeolites was reported by Pietrazah *et al.*[19] They observed temperature-dependent ESR spectra and explained them in terms of a hindered rotation of the molecule. However, it has been shown that there was no prefered axis of the rotational freedom for NO_2 adsorbed in synthetic zeolites. It is interesting that the silica-gel system shows a distinct contrast to their results in that, on the silica-gel surface, NO_2 is preferred to rotate about the O–O direction.

Structure of NO_2 on Silica Gel. In the NO_2 molecule, the odd electron is considered mainly to occupy a $4a_1$ molecular orbital constructed from nitrogen $2s$ and $2p_z$, and oxygen $2p_y$ and $2p_z$ atomic orbitals, having the form[5,13–17];

$$\begin{aligned}\Psi(4a_1) = {} & a_N(2s)\Psi_N(2s) - a_N(2p_z)\Psi_N(2p_z) + a_O(2s)\{\Psi_{O1}(2s) \\ & + \Psi_{O2}(2s)\} + a_O(2p_y)\{\Psi_{O1}(2p_y) - \Psi_{O2}(2p_y)\} \\ & + a_O(2p_z)\{\Psi_{O1}(2p_z) + \Psi_{O2}(2p_z)\}. \end{aligned} \tag{1}$$

Table 1. Magnetic parameters of NO_2 in various media

Medium	g Values			Hyperfine interaction (in MHz)				Reference
				Anisotropic components			A_{iso}	
	g_x	g_y	g_z	A_x	A_y	A_z		
$NaNO_2$(77°K)	2.0057	1.9910	2.0015	−14.77	−22.17	+37.03	+153.2	3
$NaNO_2$(293°K)	2.0059	2.0052	2.0055	− 9.5	−19.0	+28.6	+111.71	4
Ice (77°K)	2.0066	2.0020	2.0022	−17.64	−19.63	+37.55	+159.24	5
Nitromethane (77°K)	2.0047	1.9915	2.0011	−13.8	−22.1	+36.0	+146.4	6
$AgNO_3$ (77°K)	2.0090	1.9978	2.0039	−17.5	−21.8	+37.3	+157.9	7
N_2O_4 (77°K)	2.0054	1.9913	2.0015	−13.75	−19.79	+33.62	+154.61	8
Adsorbed on ZnO (77°K)	2.007	1.994	2.003	− 7.0	−21.1	+28.0	+153.1	11
Adsorbed on silica gel (77°K)	(2.004)[a)]	1.9907	(2.004)[a)]	(+9.56)[a)]	−19.12	(+9.56)[a)]	+156.1	This work
NO_2 (gas) (293°K)	2.0062	1.9910	2.0019	−18.73	−19.77	+38.50	+146.5	12

a) Averaged value for *x* and *z* components.

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The contribution of the nitrogen $2s$ orbital to the $4a_1$ orbital can be estimated from the observed isotropic part of the nitrogen hyperfine splitting constants by the following expression:

$$A_{\mathrm{iso}} = a_{\mathrm{N}}^2(2s)(8\pi/3)g\beta g_{\mathrm{N}}\beta_{\mathrm{N}}\Psi_{\mathrm{N}(2s)}(0)^2 \tag{2}$$

with:

$$\Psi_{\mathrm{N}(2s)}(0)^2 = 34.0\times 10^{24}\,\mathrm{cm}^{-3}.$$

On the other hand, the anisotropic part in the hyperfine interaction of an odd electron in the $2p_z$ component of the $4a_1$ orbital with the nitrogen nucleus can be expressed by the diagonal tensor, A_1, axially symmetric:

$$A_1 = \begin{pmatrix} -\alpha & & \\ & -\alpha & \\ & & 2\alpha \end{pmatrix} = (2/5)a_{\mathrm{N}}^2(2p_z)g\beta g_{\mathrm{N}}\beta_{\mathrm{N}}\langle r^{-3}\rangle \begin{pmatrix} -1 & & \\ & -1 & \\ & & +2 \end{pmatrix}. \tag{3}$$

However, the experimental anisotropic hyperfine tensors obtained for the immobile NO_2 molecules in the solid matrices are usually not axially symmetric but are resolved into two axially symmetric tensors, A_1 and A_2 (symmetric about the x axis). Thus:

$$A_2 + A_1 = (2/5)g\beta g_{\mathrm{N}}\beta_{\mathrm{N}}\langle r^{-3}\rangle \times \left\{ a_{\mathrm{N}}^2(2p_x)\begin{pmatrix} +2 & & \\ & -1 & \\ & & -1 \end{pmatrix} + a_{\mathrm{N}}^2(2p_z)\begin{pmatrix} -1 & & \\ & -1 & \\ & & +2 \end{pmatrix}\right\}. \tag{4}$$

A_2 has been explained as arising from the configuration interaction of the ground state with an excited state involving $2b_1 \leftarrow 1b_1$ excitation. When Dousmanis's value[20] for $\langle r^{-3}\rangle_{2p} = 22.5\times 10^{24}\,\mathrm{cm}^{-3}$ is used, one can calculate the contribution of the nitrogen $2s$ and $2p_z$ orbitals to the $4a_1$ orbital. From the estimated $a_{\mathrm{N}}(2s)$ and $a_{\mathrm{N}}(2p_z)$, the ONO angle may be calculated, assuming the usual relationship:[21]

$$\angle \mathrm{ONO} = 2\cos^{-1}(k^2+2)^{-1/2}, \tag{5}$$

where:

$$k^2 = a_{\mathrm{N}}^2(2p_z)/a_{\mathrm{N}}^2(2s).$$

The experimental hyperfine splitting constants being used, the ONO angle of the NO_2 molecule in the gas phase can be calculated to be 135.5°. In the case of the adsorbed state of the NO_2 molecule treated here, however, we cannot make such a calculation, since the x, y, and z components of the anisotropic hyperfine interaction cannot be obtained separately. However, if we compare the experimental hyperfine coupling constants with the data for NO_2 in the gas phase in Table 1, it is apparent that the magnitude of the isotropic part of the nitrogen hyperfine interaction is larger in the adsorbed state than in the gas phase, while the anisotropic part in the adsorbed state is smaller than those in the gas phase. This suggests that the contribution of the nitrogen $2s$ orbital to the $4a_1$ orbital decreases, and that the nitrogen $2p_z$ contribution may increase by adsorption from the gas phase. It is estimated, therefore, that the ONO angle may decrease by adsorption on the silica gel from the gas phase, although the change in the angle is small, *i. e.*, about 4–5°.

Conclusion

It has been found that NO_2 adsorbed on the silica-gel surface shows temperature-dependent ESR spectra. The low-temperature spectra can be explained as arising from the NO_2 molecule rotating around the O–O direction. As the temperature increases, the spectra indicate that the rotation around the other two axes become important. It is estimated from the observation that a hydrogen-bond force between the oxygen of NO_2 and OH groups on the silica-gel surface plays a part in the NO_2-silica-gel interaction. It has also been shown that the ONO angle might become smaller when NO_2 is adsorbed on the silica-gel surface from the gas phase.

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