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The Spectroscopic Study on the Dimerization of Pyridine Derivatives on the Surfaces of MgO, CaO and SrO

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The adsorption and dimerization of pyridine derivatives on MgO, CaO, and SrO were studied by ESR and visible absorption spectrometries. Adsorbed pyridine on the oxides was found to give an ESR signal of five lines and 580 nm absorption spectrum which were attributed to dipyridyl anion radical. The deuterium isotope effects for the formation of dipyridyl anion radicals were observed on MgO and CaO, but not on strong basic oxide, SrO. Methylpyridines adsorbed on MgO gave the same species as pyridine by the irradiation of light ($\lambda > 370$ nm). From these facts, the surface intermediates for the dimerization reaction were discussed. When the adsorbed species were exposed to oxygen molecule, the dipyridyl anion radicals faded away and the ESR spectra attributed to the O_2^- ion were observed.

Alkaline earth metal oxides as solid base catalysts have recently been found to show a remarkable activity and interesting selectivity for the isomerization of olefins,[1] the alkylation of phenol with methanol,[2] the conversion of benzaldehyde into benzyl benzoate,[3] *etc.* On the other hand, the formation and stabilization of negative radical ions of aromatic nitro compounds on the surfaces of MgO[4] and CaO[5] by electron transfer process are well known.

In the present work, the formation of dipyridyl anion radical by the dimerization of pyridine derivatives adsorbed on MgO, CaO, and SrO was found by ESR and visible absorption spectroscopies, and their adsorbed states were discussed.

Experimental

Magnesium oxide used in this investigation was prepared from $Mg(OH)_2$, guaranteed reagent of Kanto Chemical Co., Inc., by evacuation at different temperatures for 1 hr. Calcium and strontium oxides were from the carbonates of Merck guaranteed reagents by evacuation at 700—900 °C for 1 hr. Pyridine and α, β, γ-methylpyridines were guaranteed reagents of Wako Pure Chemical Co., Inc., distilled in a vacuum and degassed by repeating a freezing-thawing cycle several times and dried by molecular sieve. Pentadeuteropyridine was purchased from Merck Co. and purified by the same method as in pyridine derivatives.

Adsorptions were done under the vapor pressures at room temperature in a vacuum system.

A JEOL ESR spectrometer operating with 100 kHz field modulation was employed to obtain the ESR spectra. The visible absorption spectra were recorded with Shimadzu MPS-50L spectrometer by using the *in situ* quartz cell in which the pressed wafer of $Mg(OH)_2$ powder was fixed. These spectra were recorded at 20 °C.

Light irradiation was done through the pyrex glass filter by Toshiba SHL-100UH-2 ultra high pressure mercury lamp.

Results

ESR Spectra of Adsorbed Pyridine. When pyridine was introduced to MgO, CaO, and SrO evacuated at high temperature, the color of the oxide surfaces turned to purple instantly, and broad unsymmetrical ESR signals were observed as shown in Fig. 1. On MgO surface, several numbers of splittings were observed, but those splittings were obscure on CaO or SrO surface. As shown in Fig. 2, after pentadeuteropyridine (C_5D_5N) instead of pyridine adsorbed on these oxides, the sharp five splitted lines developed in the cases of MgO and CaO, but on SrO, the splitting was not clear.

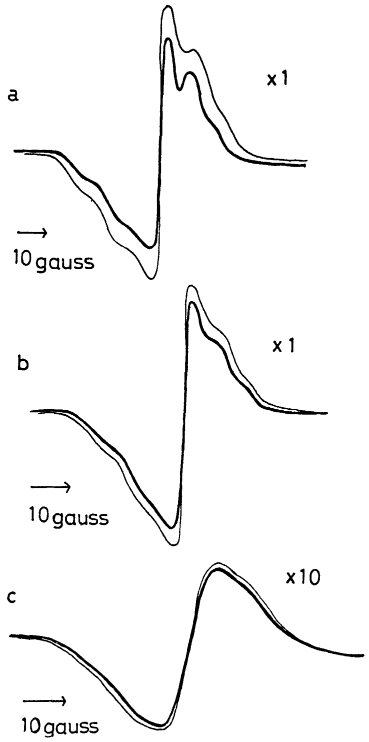


Fig. 1. ESR spectra of pyridine adsorbed on oxides. a. MgO evacuated at 600 °C, b. CaO evacuated at 700 °C, c. SrO evacuated at 900 °C, heavy line: 2 min after adsorption, weak line: 10 min after adsorption.

From the dependence of signal shape on the microwave power change, those signals were thought to be due to one paramagnetic species, and concluded to be hyperfine structure of two equivalent ^{14}N. The hyperfine coupling constants were 8.2 for MgO, 7.4 for CaO, and 7.2 gauss for SrO.

The change of the spin concentration with adsorption time was shown in Fig. 3. On MgO surface, the broader and stronger signal was obserbed on pyridine adsorption than on the adsorption of pentadeuteropy-

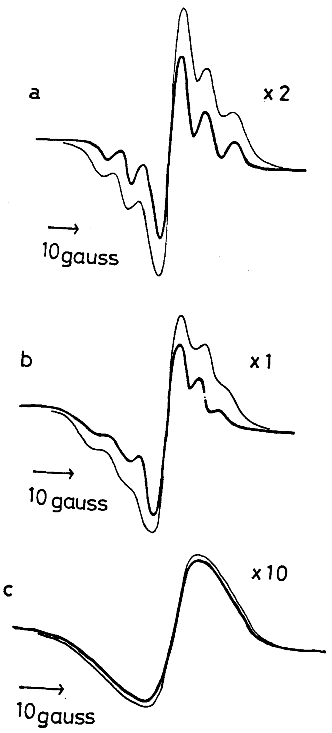


Fig. 2. ESR spectra of pentadeuteropyridine adsorbed on oxides. a. MgO evacuated at 600 °C, b. CaO evacuated at 700 °C, c. SrO evacuated at 900 °C, heavy line: 2 min after adsorption, weak line: 10 min after adsorption.

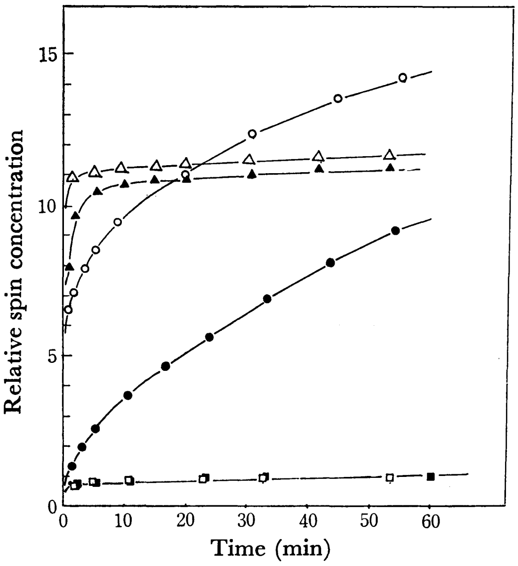


Fig. 3. Adsorption time dependence of spin concentration. ○: pyridine on MgO (evacuated at 600 °C), ●: deuteropyridine on MgO (600 °C), △: pyridine on CaO (700 °C), ▲: deuteropyridine on CaO (700 °C), □: pyridine on SrO (900 °C), ■: deuteropyridine on SrO (900 °C).

ridine. Those signals increased their intensity with adsorption time, but the shapes of two signals were very different as shown in Figs. 1 and 2.

On CaO surface, the differences in the intensity and the shape of those signals were obvious at the initial stage of the adsorption, but almost the same spectrum was observed after 20 min adsorption.

In the case of SrO, no difference was observed in the shape of spectra and spin concentration.

The Visible Spectra of Pyridine Adsorbed on MgO. The visible spectra of pyridine adsorbed on evacuated MgO were shown in Fig. 4. Those spectra had three absorption bands at 380, 470, and 580 nm.

In the reduction of pyridine by alkali metal, it is known that the formed 4,4′-dipyridyl anion radical shows the absorption at 381 and 570 nm.[6]

On MgO evacuated at high temperature, only the 580 nm band decreased remarkably. The change in 580 nm band intensity with evacuation temperature was shown in Fig. 5. It had very close correlation with the change in ESR spin density with evacuation temperature change. These facts suggest the formation of dipyridyl anion radical on MgO.

Actually, the UV spectrum of the extracted ethanol solution of adsorbed species on MgO coincided with that of 4,4′-dipyridyl.

The Visible and ESR Spectra of Methylpyridine Adsorbed on MgO. When methylpyridine adsorbed on MgO, the surface showed yellow color, but gave no ESR signal. The visible spectra of those adsorbed species

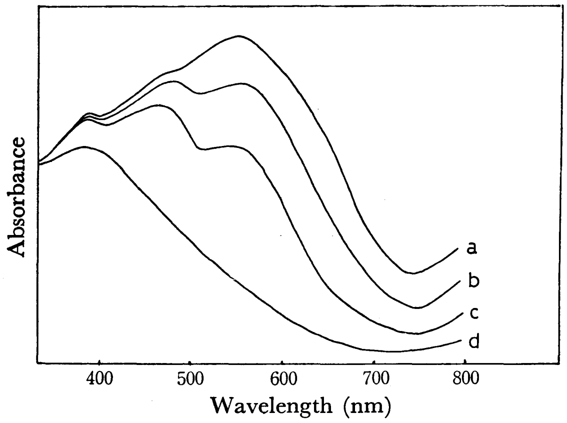


Fig. 4. Visible absorption spectra of pyridine adsorbed on MgO. a. evacuated at 600 °C, b. evacuated at 800 °C, c. evacuated at 1000 °C, d. exposed to oxygen gas.

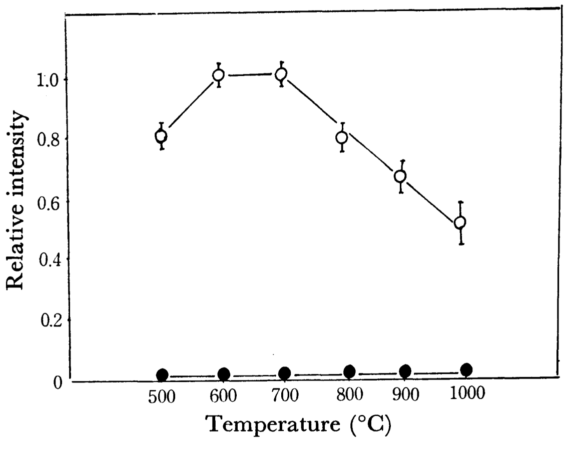


Fig. 5. Calcination temperature dependence of 580 nm band on MgO. ○: evaculated *in vacuo*, ●: heated in air.

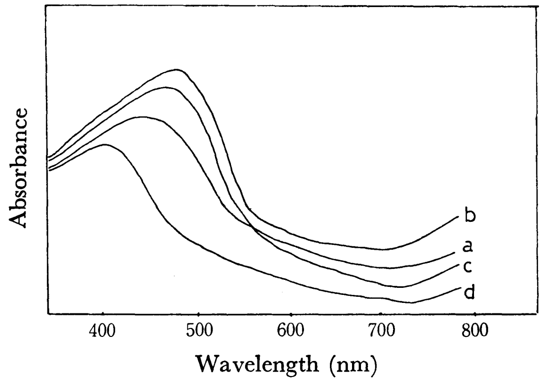


Fig. 6. Visible absorption spectra of methylpyridines adsorbed on MgO evacuated at 600 °C. a. γ-methylpyridine, b. β-methylpyridine, c. α-methylpyridine, d. exposed to oxygen gas.

are shown in Fig. 6. On any adsorbed species, only 470 nm band was observed. After the exposure to O_2 gas, this 470 nm band diminished immediately. When the methylpyridines adsorbed on MgO which showed no ESR signal were irradiated by light ($\lambda > 370$ nm), those yellow surfaces turned to purple and the intense ESR signals analogous to that in pyridine adsorption were observed.

The ESR Spectra of the Adsorbed Pyridine Derivatives Exposed to Oxygen Gas. When the pyridine adsorbed on MgO was exposed to O_2 gas, the purple color and the ESR spectrum of dipyridyl anion radical disappeared and the new broad unsymmetrical ESR spectrum with g-values at $g_1=2.076$ and 2.060, $g_2=2.008$, $g_3=2.001$ was observed at room temperature. Those g values and the shape of this spectrum agreed well with those of the adsorbed O_2^- radical on ultraviolet irradiated MgO.[7]

On CaO surface, axial symmetrical signal with $g_{//}=2.082$, $g_{\perp}=2.005$ was observed after exposure to O_2 gas. Though O_2^- ion adsorbed on CaO has never been reported, this signal would be also concluded to this ion. The O_2^- ion on SrO was not observed in spite of the disappearance of radical anion by exposure to O_2 gas. In the case of the methylpyridine adsorbed on MgO which gave no ESR signal, ESR signal of O_2^- ion appeared after the introduction of O_2 gas.

Discussion

The analysis of the ESR spectra with sharp hyperfine structure of adsorbed pentadeuteropyridine provides many informations about the electronic states of adsorbed ions, structural changes due to adsorption, and interaction with the surface. The signals shown in Fig. 2 having five line pattern are essentially due to the anisotropic interaction of the free spin of two nitrogen nuclei with each nuclear spin of unity. The Hamiltonian for this type of radical can be written in the form,

$$\mathscr{H} = \beta \cdot s \cdot \tilde{g} \cdot H + s \cdot \tilde{A} \cdot I,$$

where $\tilde{g}$, $\tilde{A}$ are tensors respectively. For axial symmetry such as an electron delocalized into a nitrogen 2p orbital, the observed hyperfine interaction α can be written as

$$\alpha^2 = [A^2 + 2AB(3\cos^2\theta - 1) + B^2(3\cos^2\theta - 1)],$$

Where A is the isotropic interaction and B is a traceless anisotropic term. If the radical is tumbling rapidly, the anisotropic interactions vanish and α becomes to A. In rigid adsorbed system, the observed hyperfine splittings can be attributed to the A and B terms, the hyperfine coupling $A+2B$ parallel to the p-orbital direction ($A_{//}$), and $A-B$ perpendicular to the p-orbital direction ($A_{\perp}$).

It is reasonable to consider that the outer four lines are parallel hyperfine, and the central line is the remaining parallel feature on which all the perpendicular components are overlapping.[8] Although a value for $(A+2B)$ has been measured, we must either measure $(A-B)$ or A independently to obtain values for A and B. Since the central line shows no resolution of $(A-B)$, some limiting values of A and B can be calculated assuming that $(A-B) < 1/2\Delta H_{pp}$. These values (gauss) are shown in Table 1.

TABLE 1.

Oxide	$(A+2B)$	ΔH_{pp}	$g_{//}$	$g_{\perp}$	A	B	$A_{iso}N$
MgO	8.2	4.0	2.0022	2.0030	4.08	2.08	—
CaO	7.4	4.2	2.0022	2.0026	3.81	1.81	—
SrO	$\simeq$7.2	$\simeq$12	2.002	2.003	$\simeq$3.8	$\simeq$1.8	—
Solution[9]	—	—	—	—	—	—	3.64

Although the values of A and B are limiting values estimated from the equation,

$$A - B = \frac{1}{2}\Delta H_{pp}$$

so large error would not be involved, since the values of ΔH_{pp} are very small. The fact that the A value of dipyridyl on MgO is slightly larger than those of CaO and SrO is due to the difference in the ionic power or Lewis acidity of Mg^{2+}, Ca^{2+} and Sr^{2+} ions. Since the A value of the adsorbed species are almost comparable to the isotropic hyperfine coupling constant of γ,γ'-dipyridyl anion radical in solution[9] (A_{iso} $N=3.64$ G), the dipyridyl negative ion on the surface is not so polarized by the crystal field.

The values of A and B for the isotropic and anisotropic interactions of the nitrogen atom can be used to obtain the s and p character of the orbital of the unpaired elcetron, since those can be written:

$$A_N = a_{2s}^2 A_0,$$
$$B_N = a_{2p}^2 B_0,$$

where a_{2s}^2 and a_{2p}^2 are the populations of the nitrogen 2s and 2p orbitals. If the values of $A_0=550$ gauss and $B_0=17.2$ gauss are used for the nitrogen atom,[10] the spin population value are shown in Table 2.

There is no difference in the spectra between adsorbed pyridine and pentadeuteropyridine (C_5D_5N) on oxides, but pyridine adsorption gives larger spin density and broader spectrum than deuteropyridine adsorption on MgO. The broadening of the spectrum in this case would be caused by the dipole-dipole interaction of the

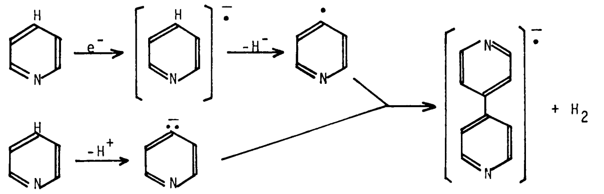
Table 2.

Oxide	a_{2s}^2	a_{2p}^2	a_{2p}^2/a_{2s}^2
MgO	0.0072	0.12	17
CaO	0.0069	0.105	15
SrO	$\simeq$0.0069	$\simeq$0.105	$\simeq$15

free spins adjoining very closely. Thus the spin density affected the shape of the spectrum. The difference in the spin density and the shape of the spectrum by the isotope labelling is evident on MgO, and this shows the isotope effect on abstraction of hydrogen or deuterium to form dipyridyl on the oxide. In the case of the adsorption on CaO, the evident isotope effect was observed in the initial stage of the adsorption, but in 20 min after the adsorption, the shape of the spectrum and the spin density became almost the same in the adsorption of pyridine or deuteropyridine. In this case, the cause of the spectrum broadening is apparently due to the increase in the spin density. On the other hand, there is no difference in the shape and spin density of adsorbed species on SrO by the isotope labelling. Since the order of the basic strength is MgO<CaO<SrO,[11] it is clear that the isotope effect becomes smaller with the increase of the basic strength, suggesting that surface oxide anion (O^{2-}) abstracts H^+ or D^+ from pyridine in the rate-determining step of the formation of dipyridyl.

The irradiation effect of light on the formation of the anion radical of phenazine on MgO was observed by Seshadri and Petrakis.[8] The anion radical formation of dipyridyl from pyridine proceeded even in dark, but the anion radical was not formed by the adsorption of methyl substituted pyridines without light irradiation. It is interesting to note that it is not necessary for the formation of the anion radical of methylpyridine dimer to irradiate with so high energy of light ($\lambda<370$ nm).

These facts suggest that both the electron transfer and H^+ abstraction are required to form dipyridyl anion radical from pyridine derivatives on alkaline earth oxides. The following scheme is proposed.



The electron transfer site on MgO was supposed to be the weakly coordinated O^{2-} ion of the surface by Che *et al.*[4b] In our scheme, the abstraction of H^+ on O^{2-} is also required. It is assured by the presence of the evident isotope effects. The abstraction of H^+ would proceed probably even on the more stabilized O^{2-} in the normal lattice than the low coordinated O^{2-} which possess electron donating ability.

On the surface of SrO, the amount of the formed dipyridyl anion radical was very small, but the isotope effect which was probably due to the abstraction of H^+ by surface O^{2-} ion was not observed.

When the adsorbed dipyridyl anion radical was exposed to oxygen gas, the anion diminished and the O_2^- ion was formed. Since the direct electron transfer to oxygen molecule on nonirradiated MgO was not observed, the expected reaction was $R^- + O_2 \rightarrow R + O_2^-$.

In the case of the exposure to O_2 gas of methylpyridine adsorbed on MgO which gave no ESR signal, the formation of O_2^- ion was also observed. From this fact, it is concluded that the adsorbed methylpyridines forms partially charge transfer complex with surface O^{2-} ion. Light facilitates this charge transfer enough to form dipyridyl derivatives through the anion radical.

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