CHEMISTRY LETTERS, pp. 891-892, 1973. Published by the Chemical Society of Japan

THE FORMATION OF ADSORBED ANION RADICAL OF DIPYRIDYL ON MAGNESIUM OXIDE AND THE ELECTRON TRANSFER TO OXYGEN MOLECULE FROM ADSORBED ANION RADICAL

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The generation of 2,2'- and 4,4'-dipyridyl anion radicals by adsorption on magnesium oxide was confirmed by means of electron spin resonance and visible spectroscopies. When the adsorbed species were exposed to air, the dipyridyl anion radical faded away and the ESR spectrum which was attributed to the oxygen molecule anion radical was observed.

On the surface of MgO, the formation of anion radicals of some electrophilic reagents is well known, but the interaction or the reaction of adsorbed anion radicals with other substances has not yet been noticed.

In this letter, the author wishes to report the formation of 2,2'- and 4,4'-dipyridyl anion radicals adsorbed on MgO and the electron transfer reaction from the adsorbed anion radical to oxygen molecule.

When 2,2'-dipyridyl was adsorbed on MgO prepared by igniting $Mg(OH)_2$ in a vacuum at 600°C for 1 hr, the color of MgO surface turned to purple blue and an intense triplet spectrum centered at g=2.0025 was observed. The observed spectrum is shown in Fig.1(a). This unresolved triplet structure is thought to be due to a single radical with hyperfine structure of nitrogen atom by the experiment of microwave power saturation. In the case of 4,4'-dipyridyl adsorption, a broad unsymmetrical singlet spectrum with a peak to peak width of about 10 gauss was observed at the same g-value of 2,2'-dipyridyl adsorbate. Those colored paramagnetic adsorbed species have a visible absorption maximum at 560 nm. The anion radical of 4,4'-dipyridyl in tetrahydrofuran has been produced by

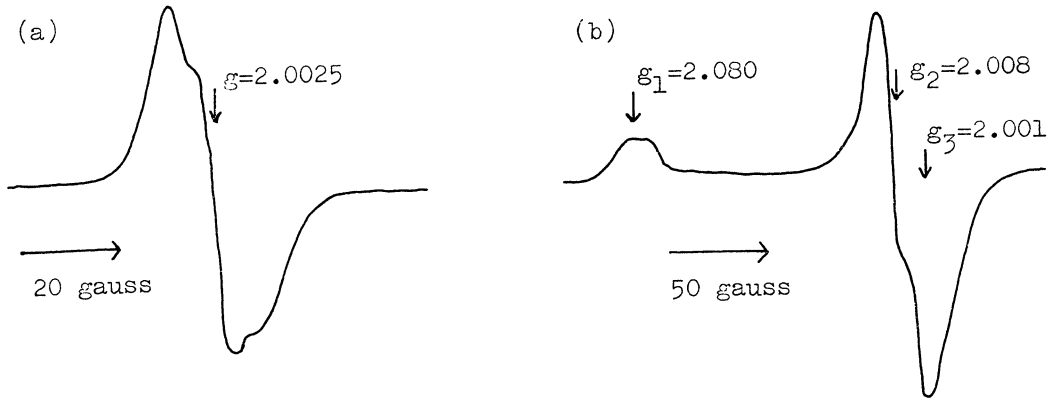

Fig.1. (a) ESR spectrum of 2,2'-dipyridyl adsorbed on MgO. (b) Spectrum at 77°K after exposure to air.

reduction with alkali metal and has two principal absorption peaks at 383 and 580 nm.[1] On the MgO surface, the 383 nm band is not clear, but the exsistence of the 560 nm band suggests the formation of dipyridyl anion radical by electron transfer process. Considering the electron donating nature of the surface of MgO, it is reasonable that the paramagnetic adsorbed species was attributed to the dipyridyl anion radical. When this blue adsorbed species was exposed to oxygen gas or air, both the blue color and the triplet spectrum disappeared and a new anisotropic spectrum with three g-values (g_1=2.080, g_2=2.008, g_3=2.001) was observed at 77°K. This spectrum is shown in Fig.1(b). Those g-values and the shape of the new spectrum agreed well with those of the adsorbed O_2^- radical on ultraviolet irradiated MgO.[2] In general, the anion radical R^- formed by alkali metal reduction immediately disappears on exposure to air. The expected reaction is $R^- + O_2 \longrightarrow R + O_2^-$. The direct electron transfer to oxygen molecule on non-irradiated MgO has never been observed. In this experiment, it was found that the negative charge of dipyridyl anion radical was transferred to oxygen molecule and the molecular oxygen anion radical was stabilized on MgO. The electron transfer reaction from dipyridyl anion to oxygen molecule is in sharp contrast to the behavior of the nitro aromatic anion radicals adsorbed on MgO which are stable in air.[3]

References

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(Received June 16, 1973)