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THE NATURE OF METHYL RADICALS ADSORBED ON AN ALUMINA SURFACE

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ESR spectra were obtained with the methyl radical adsorbed on the surface of alumina. The nature of the motion of the radical was thought to be entirely different from those trapped on a silica gel surface or porous Vycor glass; the familiar quartet hf lines were replaced by a spectrum characterized with a sextet hf structure, suggesting that the three methyl protons were no longer equivalent at the surface of alumina.

When methane was photolysed at 77 °K at the surface of alumina, the reaction system gave rise to a somewhat complex ESR spectrum quite different from those attributed to methyl radicals at the surface of silica gel or porous Vycor glass$^{1-3)}$; the familiar quartet hyperfine lines due to the methyl radical were now replaced by a spectrum characterized with a sextet hyperfine structure, suggesting that the three protons of the methyl group were no longer equivalent at the surface of alumina.

Two alumina samples were investigated as the adsorbent; Merck Co. Code No. 1097, 92 m^2/g and Nishio Ind. Co. Code AE-11, 272 m^2/g. These samples gave however essentially the same result provided that the sample was treated around 773 °K for one hour in high vacuo prior to experiments. After about a monolayer of methane molecules was introduced on the pretreated alumina, irradiations were carried out at 77 °K usually for the time less than five minutes with a low pressure mercury lamp (Ushio Electric Co., UL-200). ESR spectra were recorded at 77 °K for the photolysed product with a JEOL P-10 spectrometer(X-band) with 100 kHz field modulation.

Typical ESR spectra for methane photolysed on the alumina surface are shown in Fig. 1 where a and b are those obtained with one minute and five minutes irradiations,respectively. Close inspection of the spectra, in particular changes in the spectral intensity of the individual line with respect to irradiation time, has led us to presume that the spectra consist of the major signal A and the minor signal B, although the resolution of spectra was rather poor.

The spectrum A was thought to be a sextet with the hyperfine structure constant, 28,2 and 18,4 gauss and with the g-value of 2,0028 while the minor apparently a doublet of 46,2 gauss. These coupling constants were entirely different from those of methyl radicals (A_H=25$\sim$19 gauss) trapped on the surface of silica gel or Vycor glass$^{1-3)}$. It was then assumed that the sextet spectrum is composed of a doublet with A_H=28,2 gauss splitted by one proton, each line being further splitted into triplets with A_H=18,4 gauss by two magnetically equivalent protons (see the diagram of Fig. 1).

When deuteromethane(CD_4) was photolysed, the spectrum of Fig. 1 was replaced by a broad singlet spectrum. The fact may indicate that the observed hyperfine lines are originated from the protons of the methyl group and not from the nucleus of aluminum. Also, it seems unlikely from the following observations that the sextet signal is due to any $C_2 \sim C_3$ hydrocarbon radicals. When a mixture of methane and deuteromethane (CD_4) was photolysed on the surface of alumina, the resultant spectrum was the only superposed one; no additional spectrum was observed. Moreover, irradiations of alumina with or without ethane, ethylene, acetylene or propane resulted in spectra hardly attributable to any part of the spectra of Fig. 1.

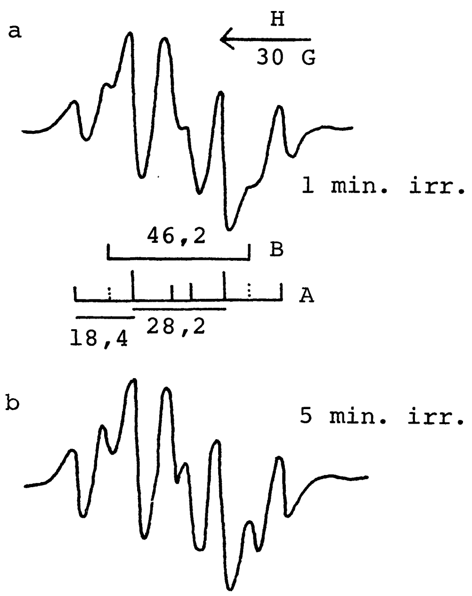

Fig. 1 ESR Spectra for Photolysed Methane on Alumina

Consequently, the major signal may be explained as due to methyl radicals in which three protons are not equivalent. Perhaps, one or two hydrogen atoms of a methyl radical must be interacting with the surface of alumina stronger than the other.

While the assignment of the minor spectrum B, showing an appearance of a doublet, is not settled yet , the present work may at least indicate that the surface of alumina is active compared with those of silica gel or Vycor glass in the sense that methyl radicals are no longer free at the surface of alumina. The mode of pretreatment of alumina has in fact shown to affect the spectral pattern and intensity for the photolysed methane in a very sensitive manner. For example, the introduction of a trace of moisture onto the surface of alumina pretreated at 773 ^{o}K made no ESR spectrum to appear for the photolysis of adsorbed methane.

References:

1) V. B. Kasanskii, G. B. Pariiskii, I. V. Aleksandrov and G. M. Zhidomirov, Soviet Physics-Solid State, 5, 473(1963).
2) J. Turkevich and Y. Fujita, Science, 152, 1619(1966).
3) N. Shimamoto, Y. Fujita and T. Kwan, Bull. Chem. Soc. Japan, 43, 580 (1970).

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