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ON THE PHOTOLYSIS OF ETHANE AND ITS DERIVATIVES ADSORBED ON ALUMINA

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The photolysis of ethane adsorbed on alumina gave rise to an ESR spectrum consisted of ten hyperfine lines instead of twelve. It was suggested that $S\text{-}\dot{C}HCH_3$ radicals are formed and that the methyl group can not rotate freely around the C-C axis.

ESR spectra of γ-irradiated ethane in inert matrices or in the presence of silica have been reported to consist of twelve hyperfine lines and interpreted as due to an ethyl radical.$^{1)}$ Accordingly, the spectra were analyzed as a quadruplet of lines arising from the three magnetically equivalent protons of the methyl group, each of which is split into a triplet as a result of hyperfine interaction with protons of the methylene group. In the previous study$^{2)}$ we have found ESR spectra of methyl radicals adsorbed on alumina quite different from those on silica$^{1)}$ or Vycor glass$^{3)}$ and suggested that the three protons of a methyl radical are no longer equivalent at the surface of alumina. Further studies were carried out therefore on the photolyzed radicals of ethane adsorbed on alumina with special interest in their motional nature as compared with that on silica.

Alumina samples employed and experimental procedures for the photolysis of ethane and ESR measurements were the same with those in the previous paper.$^{2)}$ A typical ESR spectrum for ethane photolyzed in the presence of alumina for two minutes is shown in Fig. 1. The spectrum consisted of ten hyperfine lines, unlike the silica case, with the mean line spacing of 13.3 gauss and the g-value of 2.0031. The radical species were quite stable at 77 ^{0}K but decayed in a short time at 119 ^{0}K. The spectrum was hardly analyzed as due to ethyl radicals. Instead, it could be analyzed in a way that four protons participate in the hyperfine splitting with coupling constants, 53.4, 26.7, 26.7 and 12.4 gauss, respectively. The corresponding radical would then be either $S\text{-}\dot{C}H\text{-}CH_3$ or $S\text{-}CH_2\text{-}\dot{C}H_2$ where S is a surface site.

To validate the assignment chlorine-substituted ethane derivatives such as CH_3CH_2Cl, CH_3CHCl_2 and CH_2ClCH_2Cl were photolyzed on the surface of alumina. As a result, twelve hyperfine lines or ethyl radicals were obtained from C_2H_5Cl but not from CH_3CHCl_2 which gave rise to a spectrum of ten hyperfine lines with the spaces of 12.3 gauss, viz. a type of spectrum quite similar to that of Fig. 1. In the case of CH_2ClCH_2Cl, the spectrum of ten components was not observed.

From the above observations it seems very probable that the radicals of the type, $S\text{-}\dot{C}H\text{-}CH_3$, were formed on alumina, and owing to the surface effect the methyl group rotates only restrictedly about the axis of the C-C bond resulting in inequivalent hyperfine coupling constants of the three β-protons. It is interesting to recall in this connection that an important primary process in the photolysis of gaseous ethane at 1470 Å is the elimination of a hydrogen molecule from the terminal carbon atom.[4,5]

In accordance with the motional nature of $S\text{-}\dot{C}H\text{-}CH_3$ radical as suggested above, the coupling constant of the α-proton, A_H^α, is assumed to be 26.7 gauss and those of the β-protons A_H^β, 53.4, 26.7 and 12.4 gauss, respectively. When the methyl group can not rotate freely, the value of the coupling constant of β-proton is approximately given by[6]

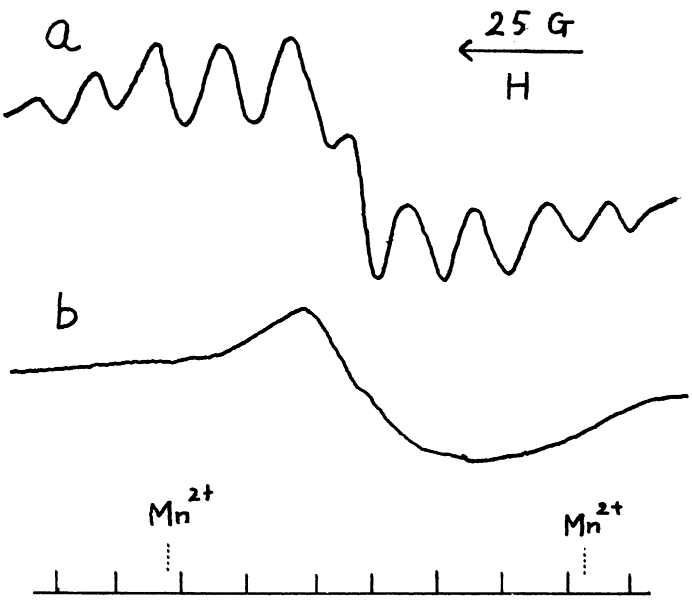

Fig. 1 ESR Spectra for Ethane photolyzed on Alumina at 77 ^{0}K (a) and for Alumina alone (b).

$$A_H^\beta = B_0 + B\cos^2\theta$$

If B_0 = 4 gauss, B = 50 gauss and θ = 8, 128 and 248^0 are respectively substituted into the equation, A_H^βs are calculated to be 53, 23 and 11 gauss. These are fairly close to the observed values.

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