# A Novel Type of Methyl Radical Trapped in Porous Vycor Glass at 77°K

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There has been interest in the study of methyl radicals trapped in various matrices.[1)] As has been reported previously, the $CH_3$ radical photoproduced from methyl iodide in the porous Vycor glass (V. G.) (Corning, ♯ 7930) was very stable even at room temperature.[1a)] According to its extraordinary stability over a wide range of temperature, Fujimoto *et al.*[1c)] have been able to study the temperature dependence of the hyperfine coupling (hfc) constant of the methyl radical stabilized on the porous V. G. surface.

Recently, in the course of our studies of the photolysis of adsorbed species on the porous V. G. surface at 77°K, we observed a novel type of methyl radical produced by the photolysis of methane; this radical was stable at 77°K and has an abnormally small hfc constant.

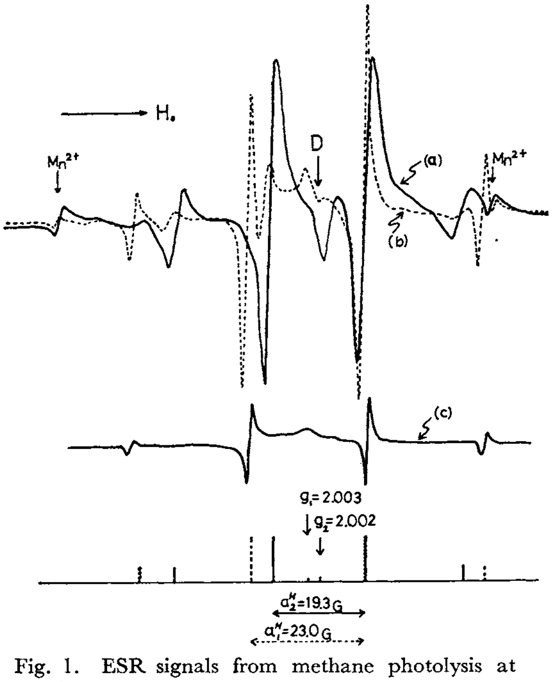

Fig. 1. ESR signals from methane photolysis at 77°K.
(a), Pure methane; (b), In the presence of iodine; (c), After slight warming of (b); $Mn^{2+}$, hfs of the standard; D, Defect signal

A porous V. G. rod (4 mm$\phi$, 20 mm in length) was preheated in an oxygen atomosphere at 600°C to remove any adsorbed organic substances. After repeating the pretreatment of the V. G. rod in a quartz sample tube, less than a monolayer amount of purified methane (usually 1/10 of a monolayer) was introduced into the evacuated sample tube at room temperature. Then the sample tube was cooled gradually from room temperature to the temperature of liquid nitrogen in order to secure a homogeneous adsorption of methane on the surface of the porous glass. Irradiation was then carried out at 77°K with the light of a low-pressure mercury lamp (Ushio Electric Co., Ltd., UL 200W). About five minutes' irradiation was enough to observe a methyl-radical signal with a good S/N ratio.

The observed ESR constants of the methyl radical were as follows:

$$|a^H| = 19.3 \pm 0.3 \text{ G}, \quad g = 2.002_3 \pm 0.0003.$$

A linewidth alternation in the proton hf lines was observed, as in the case of the $CH_3$ obtained from methyl iodide. However, unlike the normal radical from methyl iodide, this methyl radical showed an inverse linewidth alternation; *i. e.*, the higher field lines were broader (Figs. 1a and 1b). The thermal stability was also different, and the abnormal $CH_3$ decayed rapidly on slight warming, indicating a reactive character. However, this radical was efficiently trapped on the surface and did not decay, at least at 77°K.

When iodine was present during the photolysis of methane, the main signal was a normal one (Fig. 1b). This shows that iodine plays an important role in the stabilization of the normal methyl radical.

The fact that the new type of the methyl radical has a $g$-value close to that of the free electron and an extraordinary small hfc constant compared to that of the planar methyl radical ($a^H = -23$ G, $g = 2.003$) probably indicates a nonplanar (pyramidal) structure, in which an unpaired electron is in an orbital with a larger $s$-character.

The nonplanar structure may be stabilized by the strong interaction between methyl radical and the surface of porous V. G., resulting in the large linewidth. The order of the rotational correlation time of this radical was estimated to be $\tau_c = 10^{-7}$ sec. This value can be compared with that of $\tau_c = 10^{-8}$ sec of the normal methyl radical obtained from methyl iodide.

A detailed analysis is now in progress.

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1) a) J. Turkevich and Y. Fujita, *Science*, **152**, 1619 (1966); b) M. Fujimoto, H. D. Gesser, B. Garbutt and A. Cohen, *Science*, **154**, 381 (1966); *c*) G. B. Garbutt, H. D. Gesser and M. Fujimoto, *J. Chem. Phys.*, **48**, 4605 (1968); d) R. L. Morehouse, J. J. Christiansen and W. Gordy, *ibid.*, **45**, 1751 (1966).