Electron Paramagnetic Resonance of Methyl Radicals on Porous Glass Surface

Abstract. *The photolysis of methyl iodide on a porous glass surface has been studied by electron paramagnetic resonance. A large number of methyl radicals can be stabilized over a wide range of temperature. The surface of porous Vycor glass is an excellent host for trapping free radicals.*

The work of Turkevich and Fujita (*1*) has prompted us to report our work on the kinetics of the decay of methyl radicals on a porous glass surface. The methyl radical, CH_3, was formed by the photolysis of CH_3I adsorbed on Vycor porous glass (Corning Glass No. 7930) having a specific surface area of 120 m^2/g as determined by the Brunauer-Emmett-Teller method.

The surface was outgassed in a vacuum in a quartz cell at 450°C. Methyl iodide was then adsorbed from the vapor phase at room temperature, and the cell was cooled down to liquid-nitrogen temperature. The full arc of a Hanovia S-100 Alpine burner was focused on the sample, which was immersed in liquid nitrogen in a quartz dewar.

A large number of methyl radicals (about 10^{17}) were detected by the electron paramagnetic resonance (EPR) after ½ to 1 hour of irradiation on the glass surface area, 35 m^2, over a wide range of temperature. This quantity of CH_3 was large enough to study kinetics in detail.

The EPR spectrum of CH_3 was a quartet with binomial intensity ratio 1:3:3:1; the hyperfine splitting constant $A_1 = 23.4 \pm 0.2$ gauss and the *g*-factor $g_1 = 2.0024 \pm 0.0001$. The line width was very sharp, about 1.5 gauss, indicating a rapid tumbling motion of the radical. The asymmetrical intensity distribution reported by Turkevich and Fujita (*1*) and Kazanskii and others (*2*) was observed only when the surface coverage of CH_3I was low.

The intensity of the spectrum increased with time of photolysis and asymptotically approached a saturation value which seemed independent of surface coverage if the coverage was less than ten layers (about 10^{16} radicals per square meter). The manner of approach to saturation depended, however, on surface coverage and absorbed light.

The change in EPR intensity was also studied as the temperature was raised from 77°K. In general, the signal diminished in size gradually, reaching a certain value which depended on temperature and surface coverage, a cascade being observed as the temperature was changed stepwise (Fig. 1). There is a "critical" temperature, sensitive to the extent of the surface covered, at which the decay starts to take place. For example, a sample with seven layers started to decay at 100°K, whereas one with 0.7 layer did not decay at up to 120°K.

The presence of such a cascade implies that the radicals are trapped in sites with a large range (continuum) of activation energies. This is typical of solid surfaces (*3*). The presence of a critical temperature indicates a minimum depth for this continuous distribution of binding energies. The difference in critical temperature in different numbers of layers may be explained as follows. The radicals on the low-coverage surface are mostly stabilized at sites on the surface of silicate porous glass, whereas on the highly covered surface a large number of radicals are trapped in the layer of adsorbate molecules where the binding energy for the CH_3 may be somewhat less than that of the silicate surface.

The decay is probably attributable to surface diffusion of desorbed radicals, followed by recombination, for example, $2\ CH_3 \rightarrow C_2H_6$. This reaction was confirmed by a gas-chromatographic analysis, which showed that methane and ethane were the major products. The ratio of ethane to methane was always large when the surface coverage was low. The methane was probably formed during photolysis by hy-

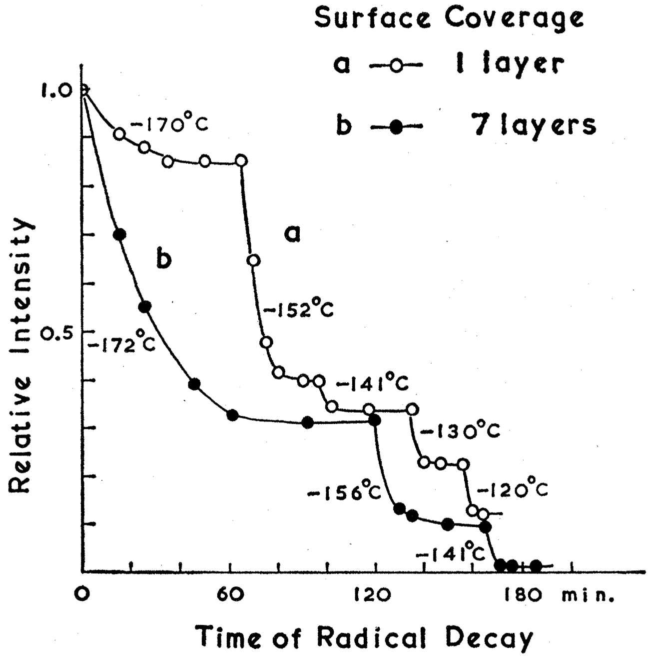

Fig. 1 (left). Decay of methyl radicals on porous glass surface at various temperatures.

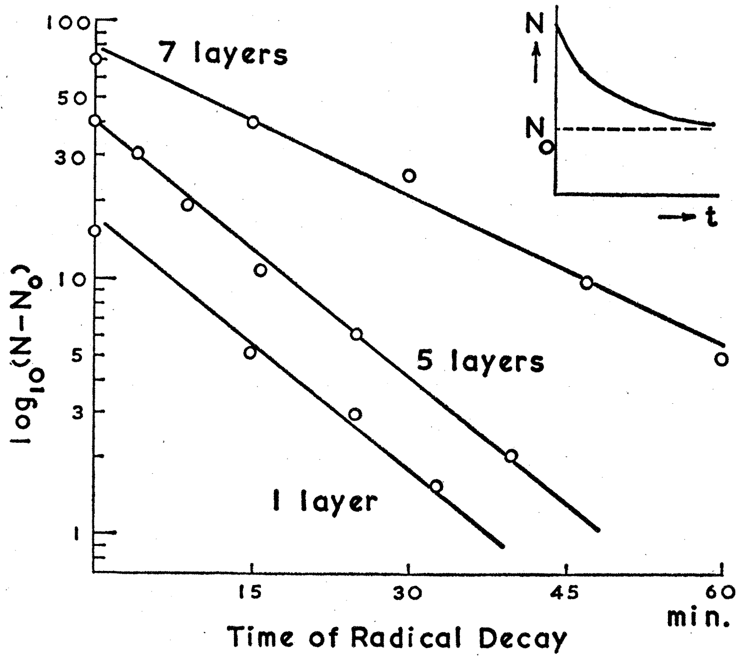

Fig. 2 (right). Decay of methyl radicals at −170°C as the logarithm of the change in ERP spectrum is plotted against time, indicating first-order kinetics, with the rate constant $k = (1 \sim 0.4) \times 10^{-1}\ min^{-1}$.

drogen abstraction by activated CH_3 (*4*). The decay follows first-order kinetics (Fig. 2), and preliminary experiments indicate that the rate constant is dependent on surface coverage. This may be interpreted by assuming that the rate is determined by the release of the radical from the surface site, and that subsequent diffusion on the surface is fast and results in a low stationary concentration of mobile radicals.

At low coverage of CH_3I (a monolayer or less), it was noted that the intensity distribution of the EPR spectrum was markedly different from the binomial one; this is explained by the presence of a second type of CH_3 radical with the hyperfine constant $A_2 = 20.2 \pm 0.4$ gauss and *g*-factor $g_2 = 2.0016 \pm 0.0005$. This second type of CH_3 radical (Me′) is clearly noticeable in the spectrum at relatively early stages of irradiation (Fig. 3), but it is not very stable at 77°K and changes to another radical (X) exhibited by those extra lines shown in Fig. 4. The radical X has not yet been identified.

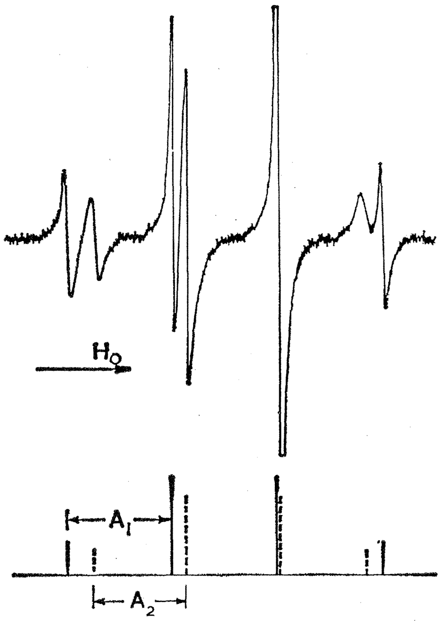

Fig. 3. The EPR spectrum of methyl radicals on the dry surface (first heated at 700°C for 48 hours), with coverage of 1 percent, observed after about 20 minutes of ultraviolet irradiation at 77°K. Extra lines and the apparent intensity anomaly of the main quartet are explained by the existence of another quartet as indicated.

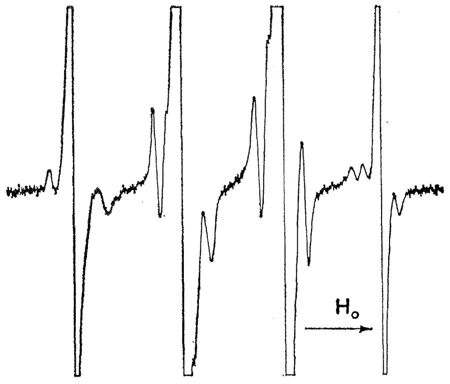

Fig. 4. The EPR spectrum of radicals on the surface, with coverage of 1 percent, stored at 77°K for more than 1 hour after irradiation.

The intensity of the Me′ spectrum increased when the porous glass was first heated at higher temperatures (700° to 850°C) for longer periods of time than the normal outgassing procedure. The appreciable reduction in the hyperfine constant indicates a charge transfer from the CH_3 to the trapping site on the silicate surface. This trapping site could be the siloxane group. In this case radical X was not detected as the signal of Me′ disappeared.

These extra lines (Me′ and X) were only observed when the surface coverage was a monolayer or less, and may be informative to identify the trapping sites on the silicate surface. For this purpose, however, it is essential to define the surface more precisely chemically. Similar spectra were also obtained by the photolysis of CH_3Br on the porous glass surface, where, in addition, the intense hydrogen atom doublet was observed.

Thus porous glass is very useful as a host material for stabilization of the free radical and has an advantage over an inert gas matrix in that liquid helium temperatures are not required. Unfortunately, the interpretation of the kinetics on such a surface is not simple because of the presence of continuum of trapping potentials. However, it is because of this continuum that the stabilization can be achieved over a wide range of temperature.

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References and Notes

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Shock-Lithification of Unconsolidated Rock Materials

Abstract. *Loose quartz grains packed around chemical explosives are forced during cratering explosions into compacted, coherent masses resembling sandstone blocks found at certain meteorite craters. Sandstone-like lumps found at the Wabar (Arabia) meteorite craters are similar to these shock-lithified sands. Shock-lithification by impact may be effected on Moon as large meteorites strike surfaces covered with rubble from earlier collisions.*

Impacts of meteorites on indurated terrestrial and lunar rock surfaces should result in overall disaggregation and fragmentation of the target materials. However, aggregation of unconsolidated materials should be a less frequent but important process associated with shock events. Using explosive shocks, Fredrickkson and DeCarli (*1*) reindurated mechanically disaggregated fragments from the Bjurbole chondrite, closely simulating its original texture. Certain brecciated achondrites may represent lithified fragments considered by some to derive from Moon's surface (*2*). I suggest that a mechanism, termed shock-lithification, may operate during repeated impacts into lunar surface rubble, by which fragments from previous impacts are welded into coherent masses; and that some such masses receive sufficient velocity for escape earthward. I now present evidence of shock-lithification during explosion cratering and terrestrial impact in support of this hypothesis.

Shock-lithification of loose materials used to tamp explosives in holes is sometimes observed after detonation, by careful examination of the environment. In 1962 a series of row-charge