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ESR Studies of Abnormal Methyl Radicals on Various Solid Surfaces

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Synopsis. Direct spectroscopic evidence is presented that strongly caged methyl iodide (or methane) molecules in *porous* surfaces are the precursors of abnormal methyl radicals. The implication of this result as concerns the nature of radical surface interaction is discussed in terms of a matrix effect.

The ESR spectra of methyl radicals trapped on solid surfaces are of interest because of their potential usefulness in surface studies. Previous independent studies using different surface types reported a number of inconsistent observations[1–3] and no collective study of these surfaces has appeared in literature. The most stable radical, the normal methyl radical (Me_n, a ≈ 2.3 mT) has been observed over a wide range of temperatures on different surfaces.[1,2,4] Interactions between the Me_n radical and surface silanol groups characterized by observable satellite lines, led to acceptable models of stabilization of this species. The formation of abnormal methyl radicals (Me_{ab}, a ≈ 1.9—2.1 mT) which are not commonly observed even at liquid nitrogen temperatures, is far less understood. Studies of this species on porous Vycor glass[1] and silica gel[2] surfaces suggested inconsistent mechanisms of stabilization. The present study of the formation of Me_{ab} radicals on various surfaces (Table 1) demonstrates a surface porosity dependence and shows for the first time, the stabilization of this species on a low temperature pretreated surface. A very low surface coverage of methyl iodide ($\approx 0.2\%$) is found necessary for their stabilization while larger coverages lead to complex radical kinetics which depend markedly on surface type, photolysis time and intensity since this radical is quickly swamped by the growth of Me_n radicals.

After the initial thermal pretreatment of the various silica surfaces under vacuum at specified temperatures (T_d) as generally described,[1–4] the surfaces were given an approximately 0.2% surface coating of methyl iodide which was left in contact for 1 h. The samples were then pumped under vacuum for 3 h at 373 K to remove physisorbed species. Studies showed that prolonged pumping at higher temperatures up to 500 K reduced only the yield of Me_n radicals but *not* the yield of Me_{ab} radicals on photolysis. Radicals were produced by UV photolysis with the full focussed radiation from a Hanovia medium pressure lamp.

A study of the yield as a function of pretreatment temperature shows enhanced yields on high T_d surfaces (Fig. 1), consistent with an expected decrease in the number of surface –OH groups. The relative yield

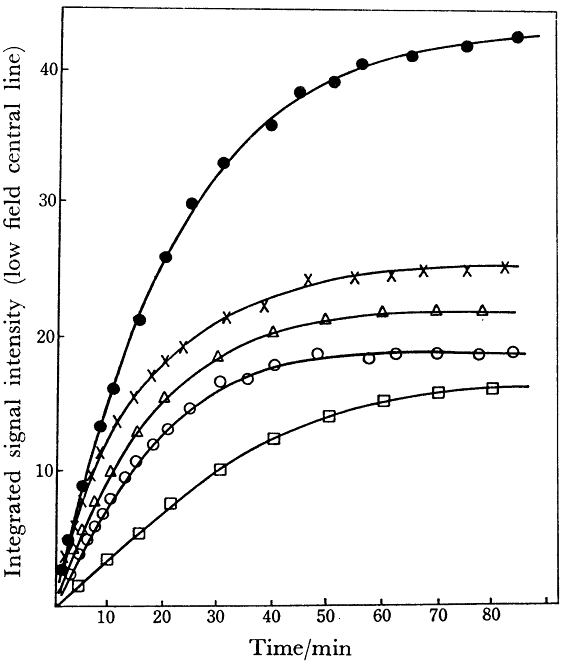

Fig. 1. The yield of abnormal methyl radicals at 77 K on macroporous silica gel surfaces pretreated at various temperatures (T_d).
T_d; ●: 1073 K, ×: 873 K, △: 773 K, ○: 673 K, □: 473 K.

TABLE 1. A LIST OF THE VARIOUS SILICA SURFACES AND THE CONSTANT RATIO OF Me_{ab} AND Me_n RADICALS STABILIZED ON THEM AFTER PROLONGED PHOTOLYSIS AT 77 K

Surface type	Manufacturer	Mean pore diameter[a] (nm)	Purity (%)		Me_{ab}/Me_n ratios at various T_d			
			SiO_2	B_2O_3	473 K	673 K	873 K	1073 K
Macroporous silica gel	Davidson/Grace Ltd.	11.5	99.8	—	7.3	15.5	23.0	35.5
Normal porosity silica gel	Hopkin & Williams Davidson/Grace Ltd.	2.2	99.8	—	0.8	2.5	4.4	6.8
Porous Vycor glass (Code 7930)	Corning Glass Works Ltd.	4.0	96.3	3	2.0	5.1	8.3	12.0
Cabosils	Cabot Carbon Ltd.	(non-porous)	99.8	—	b)	b)	b)	b)
B_2O_3 enriched glass	Glass Tubes and Components Ltd.	(non-porous)	77.5 66.8	16.5 21.8	b)	b)	b)	b)

a) Quoted by manufacturers. b) Me_n radical only observed for these cases.

TABLE 2. THE HYPERFINE CONSTANTS AND LINE WIDTH PARAMETERS (ΔH_{pp}) OBSERVED FOR ABNORMAL METHYL RADICALS STABILIZED ON POROUS VYCOR GLASS AND SILICA GEL SURFACES AT 77 K

Surface type	Pretreatment temperature / K	$a_{\mathrm{H}} \pm 0.005$ mT	$\Delta H_{\mathrm{pp}} \pm 0.005$ mT (for lines to increasing field)			
Porous Vycor glass	673	1.925	0.170	0.106	0.183	0.306
	1073	1.930	0.171	0.127	0.172	0.333
Silica gels (normal porosity and macroporous)	673	2.050	0.195	0.110	0.112	0.207
	1073a)	2.025b)	0.155	0.060	0.042	0.115
		2.080c)	0.140	0.060	0.054	0.082

a) Two types of the radical ($\mathrm{Me_{ab_1}}$ and $\mathrm{Me_{ab_2}}$) are identified on the surfaces pretreated above 870 K. b) $\mathrm{Me_{ab_1}}$ radical. c) $\mathrm{Me_{ab_2}}$ radical.

of radicals $\frac{\mathrm{Me_{ab}}}{\mathrm{Me_n}}$ obtained after prolonged photolysis of identically prepared samples of the various surface types (Table 1) increases with the surface porosity. No evidence of $\mathrm{Me_{ab}}$ radical formation on non-porous surfaces was found under any condition of sample preparation; the absence of this species on $\mathrm{B_2O_3}$ enriched glass throws some doubt on the impurity-stabilization mechanism previously suggested.1) The results strongly suggest that caged methyl iodide molecules which were not removed by prolonged pumping under vacuum at temperatures up to 500 K are precursors of $\mathrm{Me_{ab}}$ radicals.

It has been shown previously5) that $\mathrm{Me_n}$ radicals trapped on various silica surfaces exhibit identical spectral parameters (ignoring small distortions caused by second order effects). The parameters observed for $\mathrm{Me_{ab}}$ radicals (Table 2) however, depend markedly on surface type; these suggest that $\mathrm{Me_{ab}}$, rather than $\mathrm{Me_n}$ radicals,4) are more effective labels for surface studies. These spectral differences may be explained by a matrix effect6) in which interactions between the radical and the matrix particles can restrict radical rotations (causing line broadening) and reduce the hyperfine constants as compared to the $\mathrm{Me_n}$ radical. Since porous Vycor glass also contains boron (^{11}B has I=3/2), coupling with the quadrupole moments could produce the additional line broadening observed for $\mathrm{Me_{ab}}$ radical on this surface. This interpretation is in accord with the work of Fujita *et al.*7) who showed that the reduced hyperfine constants observed for $\mathrm{Me_{ab}}$ radicals on porous Vycor glass and other matrices represent charge transfer to their environments. It can thus be deduced from our data that the charge transfer effect is greater for porous Vycor glass than for silica gel surfaces.

Two species of the abnormal radical, namely $\mathrm{Me_{ab_1}}$ and $\mathrm{Me_{ab_2}}$ are identified on silica gel pretreated above 870 K (Table 2). It is suggested that $\mathrm{Me_{ab_2}}$ radical observed only on these surfaces interacts with siloxane bridges known to occur under these conditions. A variable temperature study shows that $\mathrm{Me_{ab_2}}$ is relatively unstable and is not observed even under continuous photolysis at 98 K. Previous authors2) have suggested the presence of the $\mathrm{Me_{ab_2}}$ radical but their results have been open to various interpretations such as a further splitting of $\mathrm{Me_{ab_1}}$ spectrum by a nuclear spin I=1/2 which produces line separations increasing to high field due to second order effects. This is the first study to identify this radical unambiguously. Matrix effects probably preclude resolution of $\mathrm{Me_{ab_2}}$ radical on porous Vycor glass.

Fujieda *et al.*3) previously reported that the ESR spectra of methyl radicals produced from one monolayer of methane adsorbed on alumina surfaces show a partially resolved sextet structure and deduced that the three methyl protons in this system are not equivalent, one or two interacting more strongly with the surface than the other. However, the present study shows that by pumping off weakly adsorbed $\mathrm{CH_4}$ a well resolved quartet (a $\approx$2.0 mT) is observed. Thus the non-equivalence of the 3 methyl protons suggested by Fujieda arises from their experiment conditions and could be due to dipolar interactions and other secondary causes.

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