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Stabilization of Normal Methyl Radicals after γ-Radiolysis at 300 K

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Synopsis. Radiolytically produced normal methyl radicals are stabilized on solid surfaces at room temperature for the first time. The remarkable stability of this species on basic and neutral alumina surfaces at 300 K and in the presence of oxygen makes this system potentially useful as an intermediate in organic synthesis.

Since Turkevich and Fujita[1)] first published the stabilization of normal methyl radicals (Me_n, $a \simeq 2.3$ mT) on porous Vycor glass, there have been several investigations of this system.[2–5)] Such studies have shown that unlike the photolytically produced Me_n radical, the Me_n radical produced radiolytically at liquid nitrogen temperatures is neither observed at room temperature nor is the radical observed directly after radiolysis at room temperature. No suggestion has been put forward to explain this anomaly. In the course of our studies on the radiolysis of adsorbed species on alumina surfaces we succeeded in stabilizing Me_n radicals directly after radiolysis of adsorbed methyl iodide on basic and neutral alumina at 300 K. The line widths, hyperfine splitting and g values are $\simeq 0.10$ mT, 2.25 ± 0.005 mT and 2.0021 ± 0.0002 respectively, in good agreement with known data for the photolytically produced radical stabilized on other adsorbents.

Chromatographic grades aluminium oxides obtained from Hopkin and William (codes 128400-active basic, 128700-active neutral and 1287.50-acidic), Merck (codes 1076-basic, 1077-neutral and 1078-acidic) British Drug House (code 15139-neutral) and Woelm of Germany (code W200-basic) were used in this investigation; all were specified as γ-alumina and Brockmann activity=1. These oxides were initially heated in oxygen at 680 K and then under vacuum at $\simeq$900 K for 5 h. The samples were given an approximate 2% surface coating of methyl iodide at room temperature and sealed in vitreosil/pyrex ESR cells as generally described by other workers.[1–4)] Surfaces given larger MeI coverages gave an unstable broad ESR signal (on radiolysis) having a line width of $\simeq$1.5 mT and a mean life time of $\simeq$2 h at room temperature. Samples were mixed thoroughly and were normally given a γ-dose of 250 krad, at room temperature, from a ^{60}Co source, although a dose of 100 krad produced signals having an adequate signal to noise ratio. Irradiation induced defects in the cells were flame annealed from the cavity section before transferring the sample. ESR measurements were made on a Decca X-3 spectrometer, all the hyperfine components of the spectrum being measured with respect to line widths, splittings and intensities.

The Me_n radical thus formed on basic and neutral alumina surfaces was found to be remarkably stable over several months at room temperature and we were able to study its reactivity towards various additives (Table 1). The results are contrary to those observed by Turkevich and Fujita[1)] who found that the Me_n radical produced by photolysis of methyl iodide adsorbed on porous Vycor glass at room temperature reacted very rapidly with oxygen and hydrogen.

The decay of the Me_n radical *in vacuo* as a function of temperature (Fig. 1), shows a cascade effect at each temperature with an initial relatively rapid decay followed by a levelling off to a value dependent on the temperature. This result suggests that there is a continuium of activation energies for decay rather than the discrete activation energies proposed by Joppien and Willard.[3)] This interpretation is in accord with that of Fujimoto *et al.*[2)] who observed such a cascade effect in the decay of photolytically produced Me_n radicals on porous Vycor glass above 77 K.

Measurements of the line widths at liquid nitrogen temperatures showed a generalised broadening effect

Table 1. The effect of additives on the yield of Me_n radicals formed by radiolysis of adsorbed methyl iodide on basic-Al_2O_3 at 300 K

Additive	Me_n Signal intensity/%[c)]	
	a)	b)
Oxygen	95	96
Hydrogen	74	81
Water vapour[d)]	13	72

a) Additive present during radiolysis. b) Additive introduced after radiolysis. c) Yield of unadulterated sample *in vacuo*=100%. d) These measurements were made at 260 K to compensate for the dielectric loss of H_2O.

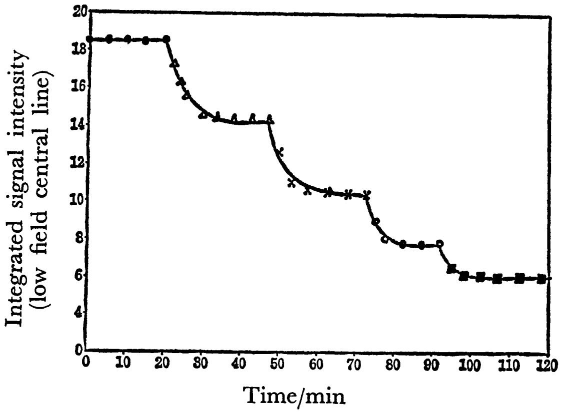

Fig. 1. The decay at elevated temperatures of Me_n radicals radiolytically produced on basic-Al_2O_3 at 300 K.

●: 293 K, △: 323 K, ×: 373 K, ○: 423 K, ■: 473 K.

(of all the component lines) to a value of $\simeq 2.5$ mT, suggesting that unlike the Me_n radical trapped on silica gel[5,6] and on porous Vycor glass,[1] the species on alumina is immobilised on the surface.

Failure to observe the radical at room temperature on acidic alumina and other acidic surfaces such as silica gel and porous Vycor glass, suggests that the radical is perturbed under these conditions. Although it is believed that the acidity of the latter surfaces is very much weaker than that of γ-alumina, significantly increased acidity of these surfaces as a result of exposure to ionizing radiation has been reported previously.[7] This irradiation induced acidity may well preclude the stabilization of Me_n radical. A study of these surfaces by the present authors[8] shows that an irradiation induced defect interacts with Me_n radicals stabilized on them at liquid nitrogen temperature to produce line broadening and other secondary effects, and persists to above 300 K; this has a g value of 2.0022 ± 0.0001, suggesting that it may be due to trapped electrons. The absence of such a defect signal on the alumina surfaces would enhance stabilization of the radical.

The above results, showing the remarkable stability of radiolytically produced Me_n radical on alumina surfaces at room temperature and in oxygen, make this system potentially useful as an intermediate in organic synthesis. A more detailed study of the site or mechanism of stabilization of this species and of the effect of other additives on yield is in progress.

References

1) J. Turkevich and Y. Fujita, *Science*, **152**, 1619 (1966).

2) M. Fujimoto, H. D. Gesser, B. Garbutt, and A. Cohen, *Science*, **154**, 381 (1966).

3) P. K. Wong and J. E. Willard, *J. Phys. Chem.*, **72**, 2623 (1968); G. R. Joppien and J. E. Willard, *ibid.*, **78**, 1391 (1974).

4) G. B. Garbutt, H. D. Gesser and M. Fujimoto, *J. Chem. Phys.*, **48**, 4065 (1968); G. B. Garbutt and H. D. Gesser, *Can. J. Chem.*, **48**, 2685 (1970).

5) D. Oduwole, J. D. Barnes, and B. Wiseall, *J. Chem. Soc., Chem. Commun.*, **1978**, 164.

6) C. L. Gardner and E. J. Casey, *Can. J. Chem.*, **46**, 207 (1968).

7) C. Barter and C. D. Wagner, *J. Phys. Chem.*, **68**, 2351 (1964).

8) To be published.