

Abnormal Methyl Radicals on Alumina Surfaces

John David BARNES, Mahendra Aruind TRIVEDI, Duro Abimbola ODUWOLE, and Barrie WISEALL

Department of Chemistry, City of London Polytechnic, Jewry Street, London EC3N 2EY.

[†]Department of Chemistry, Queen Mary College, Mile End Road, London E1 4NS.

(Received April 17, 1984)

Synopsis. The ESR spectrum of abnormal methyl radicals on alumina surfaces is found to be symmetrical at low surface coverages. Possible mechanisms for the formation of these radicals are presented.

Fujieda *et al.*¹⁾ have interpreted the ESR spectra of methyl radicals produced by the photolysis of methane adsorbed on alumina surfaces as indicating that the three methyl protons are not equivalent and that one is interacting more strongly with the surface than the other two. In an earlier paper²⁾ concerned with the stabilisation of abnormal methyl radicals (Me_{ab}) on silica gel surfaces we suggested that this observation was due to concentration effects arising from the relatively high surface coverages employed and that strongly caged adsorbate molecules are precursors of the abnormal radical. The present study examines this problem in more detail and suggests a possible mechanism for the production of Me_{ab} .

Chromatographic grade neutral activated alumina powder, Brockmann grade 1, was obtained from British Drug House (BDH). Prior to sample preparation, alumina powder was heated in air at 537 K to oxidize and remove any organic impurities; it was then dehydrated at a predetermined temperature (T_d) for 4 h *in vacuo*. Excess iodomethane was adsorbed onto the surface at room temperature and the sample pumped off for 1 h. The samples were sealed in Vitreosil/Pyrex ESR cells as previously described.^{3–6)} Methyl radicals were produced by UV photolysis at 77 K using a medium pressure Hanovia lamp. ESR measurements were made on a Decca X-3 spectrometer employing a microwave frequency of 9270.28 ± 0.01 MHz with a reflection cavity fitted with a proton resonance probe for field determination and modulated at 100 kHz.

A preliminary study showed that Me_{ab} radicals could be obtained only from strongly pumped off alumina samples prepared above a T_d of 673 K and were not stable above 77 K. Contrary to the observation of Fujieda, the Me_{ab} radical ESR spectrum was found to be symmetrical with approximate line intensities of 1:5:5:1 and line widths of 0.211, 0.143, 0.132, and 0.198 mT respectively from low to high field. The Me_{ab} radical concentration at first increased with photolysis time but eventually attained a steady state. The yield as a function of T_d is shown in Fig. 1 and confirms that these radicals are not produced on samples prepared below a T_d of 673 K even after prolonged photolysis. Their absence may be attributed either to the lack of sites of stabilization for the radicals and/or to the lack of sites of absorption for the iodomethane. Since molecular water remains strongly adsorbed onto alumina surfaces up to 573 K,^{7,8)} it is possible that at the lower temperature iodomethane molecules cannot be strongly adsorbed in the first step and are completely removed in the pump-off process. The Me_{ab} radical

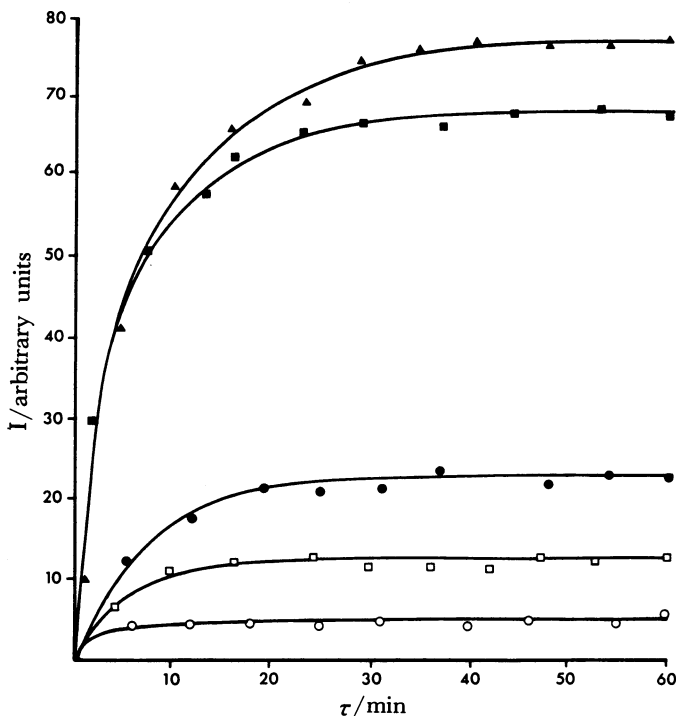


Fig. 1. The yield of abnormal methyl radicals at 77 K on alumina surfaces pretreated at various temperatures. I is the integrated signal intensity of the low field line in the methyl radical spectrum and τ is the photolysis time.

T_d ; ■: 1173 K, ▲: 1073 K, ●: 973 K, □: 873 K, ○: 773 K.

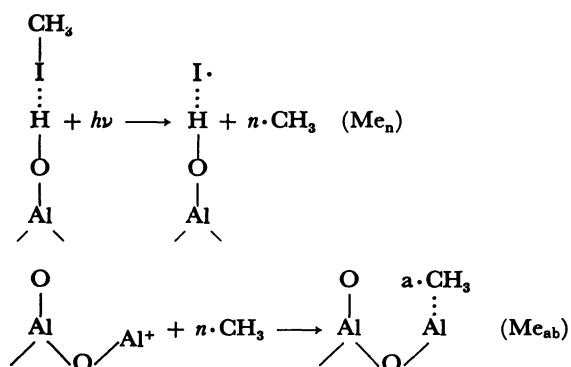
yield increased with T_d from 673 K to 1073 K and then decreased at 1173 K. On increasing the T_d above 673 K, although the surface hydroxyls which are thought to be the sites of adsorption may decrease⁹⁾ the surface sites of stabilization would increase and result in a higher concentration of Me_{ab} radicals. However, at 1173 K, bulk movement in the alumina matrix may result in the sintering of pore walls, a reduction in pore volume and a large reduction in surface area which must reduce the number of sites of stabilization.

The formation of Me_{ab} radicals on alumina surfaces can be accounted for in two ways. The first involves the sites of adsorption and it is suggested that iodomethane is more strongly adsorbed by those surface hydroxyls remaining on the surface. The stronger adsorption may result in a change of planar methyl in iodomethane to nonplanar methyl, which on UV photolysis yields Me_{ab} radicals. If this was true, then since alumina surfaces have at least 5 different types of surface hydroxyl group⁷⁾ it should be possible to observe 5 different types of Me_{ab} radical and to vary their relative concentrations with T_d .

The second and more likely possibility involves the sites of stabilization of the radical once formed. Normal methyl radicals (Me_{n} , $a=2.3$ mT) produced

during photolysis stabilise upon electron deficient aluminium ions exposed during dehydration of the surface to exhibit a single Me_{ab} radical spectrum ($a = 2.08 \text{ mT}$). The attraction of the unpaired electron of the Me_{n} radical closer to the site of stabilisation, effectively changes the ESR characteristics of the methyl radical spectrum. Support for this mechanism is found in the work of Fujita *et al.*¹⁰ who suggest that a reduction in the hyperfine splitting constant indicates charge transfer to the environment.

The production of Me_{ab} may be represented schematically as:



References

- 1) S. Fujieda, M. Setaka, and T. Kwan, *Chem. Lett.*, **1972**, 43.
- 2) D. A. Oduwole and B. Wiseall, *Bull. Chem. Soc. Jpn.*, **53**, 3037 (1980).
- 3) J. Turkevich and Y. Fujita, *Science*, **152**, 1619 (1966).
- 4) M. Fujimoto, H. D. Gesser, B. Garbutt, and A. Cohen, *Science*, **154**, 381 (1966).
- 5) P. K. Wong and J. E. Willard, *J. Phys. Chem.*, **72**, 2623 (1968); G. R. Joppien and J. E. Willard, *ibid.*, **78**, 1391 (1974).
- 6) 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).
- 7) J. B. Peri, *J. Phys. Chem.*, **69**, 211; 220 (1965).
- 8) D. J. Norfolk and T. Swan, *J. Chem. Soc. Faraday Trans.*, **73**, 1454 (1977).
- 9) F. H. Van Cauwelaert, J. R. Van Assche, and J. B. Utterhoeven, *J. Phys. Chem.*, **74**, 4329 (1970).
- 10) Y. Fujita, T. Katsu, and M. Sato, *J. Chem. Phys.*, **61**, 4307 (1974).