E.S.R. Studies of Encapsulated Methyl Radicals

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γ-Irradiation, at 77 K, of methane encapsulated in zeolite 3A forms CH_3 radicals which are stable in air up to *ca.* 195 K.

The encapsulation of methane and hydrogen in zeolites has aroused interest because of its potential for the storage of these gases.[1–3] During the course of methane encapsulation studies,[4] we realized that while e.s.r. studies had been made of methyl radicals adsorbed on zeolites,[5,6] no such studies had been done for methyl radicals arising from encapsulated methane.

Unlike adsorption which is a surface phenomenon, encapsulation involves forcing the gas molecules under high temperature and pressure conditions into the pores of the zeolite. The resultant encapsulate is stable at ambient temperatures but the gas can be released at will by once more heating the zeolite. It seemed possible that γ-irradiation of encapsulated methane might lead to both methyl radicals and hydro-

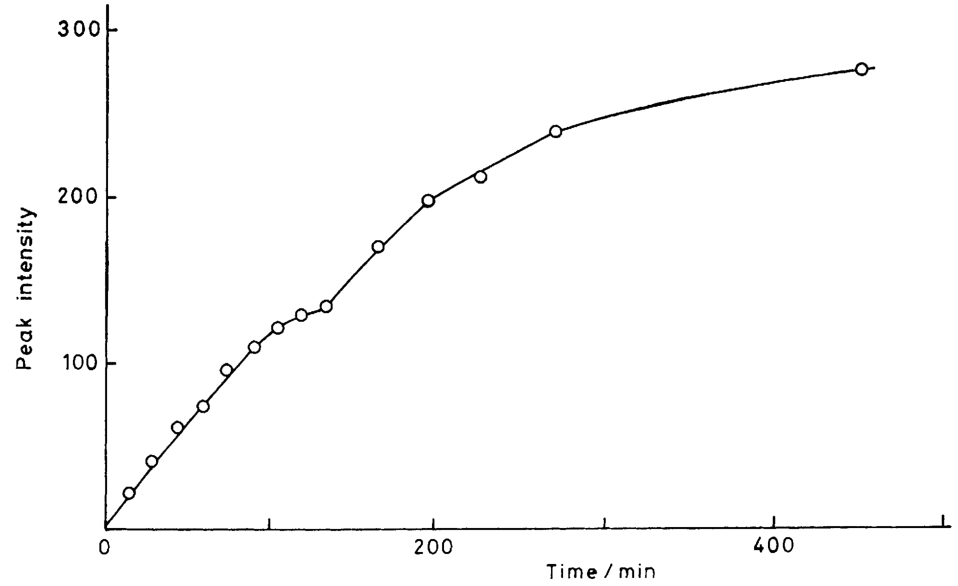

Figure 1. Methyl radical build-up as a function of total irradiation time.

gen atoms being simultaneously formed and trapped within the zeolite cage. When we irradiated a Linde 3A 'methane loaded' (to 6% by weight) zeolite at −196 °C we found that this was indeed the case. A ^{60}Co source was used for the irradiation and the samples received a total dose of about 1 Mrad.

The samples were prepared for irradiation as follows: the zeolite, after activation at 350 °C under vacuum, was loaded with methane using encapsulation pressures of 0.7×10^8 to 4.1×10^8 Pa and encapsulation temperatures of 250—350 °C; it was then transferred to a quartz e.s.r. tube and sealed under vacuum (10^{-3} Pa) before irradiation took place. A blank consisting of activated zeolite was similarly prepared and irradiated. During and following irradiation, the samples were stored in liquid nitrogen.

E.s.r. spectra were recorded on a Varian E-3 e.s.r. spectrometer employing 100 kHz modulation over the temperature range −196 to 25 °C.

At −196 °C the e.s.r. spectrum of the irradiated 'blank' zeolite sample consisted of a broad signal centred at *g ca.* 2.008 and a very weak H doublet. The production of paramagnetic centres giving rise to singlet e.s.r. signals in irradiated zeolites had been previously reported by several workers[5—12] and has been attributed to the formation of Na_4^{3+} (F centres) and V(hole centres). On warming the sample to room temperature, the singlet rapidly decayed leaving a weak complex residual signal that persisted at room temperature.

The e.s.r. spectrum of the 'loaded' zeolite at −196 °C after irradiation consisted of a quartet [$g = 2.002(2)$] arising from the methyl radical and a weak H doublet. The signal due to the quartet was stable for several days at temperatures as high as −78 °C but decayed rapidly at room temperature.

The H doublet was also stable for several days at −196 °C but disappeared at −78 °C. Since the intensity of the doublet varies from sample to sample and since the doublet also appears in the blank, it must therefore arise at least in part from residual water as well as from methane dissociation.

The methyl quartet exhibits a slight asymmetry. The asymmetry is reminiscent of that observed by previous workers for methyl radicals stabilized on porous Vycor glass[13,14] or adsorbed on silica[14] and has been ascribed by these workers to a small concentration of an abnormal methyl radical (Type I). In our case, however, the asymmetry may equally be due to the underlying signal from the zeolite itself. No evidence was found for the presence of the abnormal methyl radical, Type II, reported by Shiotani *et al.*[6]

The build-up of methyl radicals as a function of irradiation time was also studied (Figure 1). A small plateau was noted after *ca.* 100 min of irradiation but with further irradiation the concentration of methyl radicals began to increase again.

The reason for this initial anomalous plateau is not apparent. Over the same time period, the intensity of the signal due to the zeolite itself shows only a small steady increase; thus the plateau does not appear to be caused by the underlying blank signal. One possibility is that in the initial stages of irradiation, the methyl radicals are being partially deactivated by reaction with a radiation induced lattice defect; and that only after these defects are essentially 'titrated' with methyl radicals, can the methyl radical concentration rise again. Since, however, the same plateau was observed with samples that had been irradiated and then warmed to room temperature several times previously, one must also postulate that the structural feature giving rise to the lattice defect is regenerated when the sample is warmed.

A brief study of the decay of the methyl radical at 0 °C and −20.5 °C was also made. Attempts to fit the decay data to first and second order rate laws were unsuccessful; analysis of the decay, however, is complicated by the underlying signal from the blank which is itself also undergoing a decay and transformation process. The decay process of the methyl radicals did not exhibit the 'cascade' effect that had been previously reported for methyl radicals stabilized on Vycor glass[13,14] or on basic alumina.[15—17]

That the methyl radical is indeed trapped within the pore of the zeolite rather than adsorbed on an outer surface is demonstrated by the fact that when an irradiated sample, cooled in a dry ice–methanol bath was opened to the atmosphere, the methyl quartet signal remained stable and degraded only very slowly over a period of several days probably as the result of slow oxygen diffusion into the pores. In comparison, it has been found that when CH_3 radicals, surface stabilized on Vycor glass, were exposed to O_2, they rapidly disappeared.[18] The only methyl radical system of comparable stability previously reported is that described by Oduwole *et al.*[16,17] They found that methyl radicals adsorbed on basic or neutral alumina were stable in the presence of small amounts (10 mmHg) of oxygen and hydrogen; and they believed this stability was due to the radical being immobilized at an inaccessible site on the alumina surface.

Several attempts were made to stabilize the methyl radical on the surface of the Type 3A zeolite in order to compare its reaction with oxygen to that of the encapsuled radical. A thoroughly degassed sample (*ca.* 10^{-3} Pa, 350 °C) was equilibrated with CH_4 at 77 K, evacuated to 0.02 Pa and sealed off. The sample, while still immersed in liquid nitrogen, was irradiated as before (^{60}Co *ca.* 1 Mrad dose) but only the signal associated with the blank zeolite was observed. This is probably due to the small exterior surface of the 3A zeolite sample and the small amount of methane which can be adsorbed. By comparison, the 4A zeolite used by the previous workers[5,6] to stabilize Me radicals allows the methane molecule to penetrate the pores freely and thus presents a much greater surface for adsorption.

Very recently, Griffith *et al.*[19] have reported that they have observed very weak methyl e.s.r. signals in naturally occurring lepispheric cherts after heating. They have explained this signal as arising from organic species trapped in molecular sized holes in the silica substrate. The presence of such a signal, albeit weak, at ambient temperatures is very promising as it would suggest that with suitable modifications of the zeolite structure, systems might be developed in which the methyl radical is encapsulated at room temperature, and yet could be released by heating the zeolite to higher temperatures. Such 'bottled' methyl radicals could obviously have considerable potential utility as polymerization initiators.

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