Letters

Germanium-73 nuclear magnetic resonance spectra of GeO_2 dissolved in water

Germanium dioxide occurs as a component of natural minerals and meteorites.[1] It has been widely used as a starting material in inorganic synthesis and recently in the synthesis of organogermanium compounds.[2,3] For these reasons the possibility of detecting GeO_2 by means of n.m.r. spectroscopy is intriguing not only from a theoretical but also from a purely practical point of view.

Usually, a ^{73}Ge n.m.r. signal can only be observed if the charge distribution around the germanium nucleus has spherical symmetry, *e.g.* for symmetrically substituted tetrahedral derivatives of the type GeR_4 as well as for octahedral complexes GeX_6.[4] This is due to the unfavourable n.m.r. properties of the ^{73}Ge nucleus, *i.e.* spin $I = \frac{9}{2}$ and very low resonance frequency (12.56 MHz in a field of $B_0 = 8.46$ T; for further details see refs. 5—7).

Earlier attempts to observe ^{73}Ge n.m.r. spectra for GeO_2 dissolved in concentrated NaOH {suggesting the formation of $[Ge(OH)_6]^{2-}$} were unsuccessful.[5] These negative results were also confirmed by the present work. However, we were able to detect a relatively narrow ^{73}Ge resonance at -16.7 p.p.m. (linewidth at half height, $\Delta\nu_{\frac{1}{2}} = 22$ Hz) for a neutral solution of GeO_2 in ^2H_2O [see Figure (*a*)] despite the considerably lower solubility of GeO_2 under these conditions. The small linewidth (implying high symmetry of the charge distribution around Ge) and substantial downfield shift for the observed signal as compared with the resonances of alkoxogermanes ($\delta = -37.8$ to -49.7 p.p.m.[7]) allow one to assign this signal to $Ge(OH)_4$. This is consistent with earlier conclusions[1] and with ^{29}Si n.m.r. data for analogous silicon derivatives. For instance, there is an acceptable correspondence between the observed ^{73}Ge n.m.r. chemical shift and the value (-23 ± 13 p.p.m.) predicted on the basis of the correlation between the ^{73}Ge and ^{29}Si chemical shifts $[\delta(^{73}Ge) = 88.7 + 1.6\delta(^{29}Si)]$[8] and the ^{29}Si chemical shift of $Si(OH)_4$ (-70.0 p.p.m.).[9]

The solubility of GeO_2 in water increases substantially in the presence of triethylamine,[10] indicating some kind of complex formation. Indeed, we have observed a ^{73}Ge n.m.r. signal at -269.1 p.p.m., replacing that at -16.7 p.p.m. [Figure (*b*)]. The strong high-field shift ($\Delta\delta = -252.4$ p.p.m.) suggests the formation of a six-co-ordinate germanium complex.[4,11] Because we have not observed (by means of ^1H, ^{14}N, and ^{73}Ge n.m.r. spectroscopy) any interaction between $Ge(OEt)_4$ and 2,2′-bipyridine, we prefer to assign this signal to $[Ge(OH)_6]^{2-}$ type anions rather than to a $Ge(OH)_4(NEt_3)_2$ complex. The former can arise as a result of the increased pH of the solution ($pK_a = 11.0$ for NEt_3). It is noteworthy that a very weak signal was detected despite the high content of GeO_2 in the solution. A resolution-enhanced spectrum indicates that the observed resonance consists of at least four ($\delta = -262.5$, -269.3, -274.5, and -282.2 p.p.m.) closely spaced signals. It is reasonable to assign these to six-co-ordinate $-O-Ge(OH)_5{}^{2-}$ end-groups of oligomeric germoxanes of different length and structure.

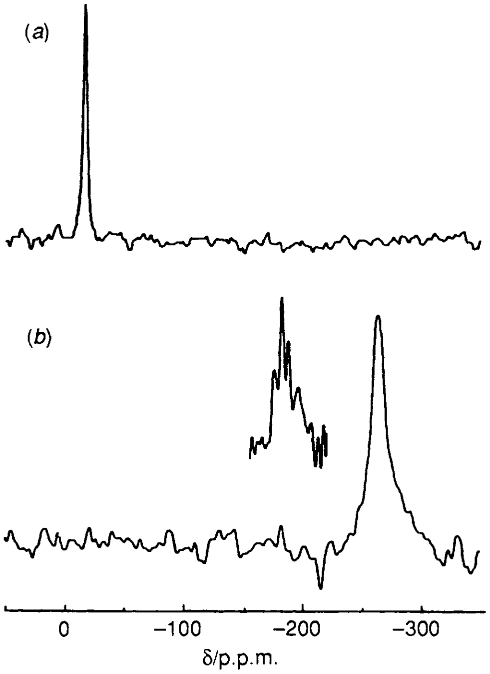

Figure. 12.56-MHz ^{73}Ge N.m.r. spectra of GeO_2 dissolved (*a*) in ^2H_2O and (*b*) in a 3:1 mixture of ^2H_2O and NEt_3, obtained in 5-mm sample tubes at 303 K overnight (*ca.* 10^6 scans) using a Bruker WM-360 spectrometer. Exponential multiplication (line broadening = 30—50 Hz) was used, except for the upper trace of spectrum (*b*) and when the linewidths were estimated

The ^{29}Si n.m.r. data for SiO_2 dissolved in water[9,12,13] and the results obtained in this work indicate that among the factors substantially increasing the relaxation rate of ^{73}Ge and, therefore, precluding the observation of the ^{73}Ge n.m.r. signals of the germoxane chain in alkaline solutions, the most plausible are (1) substantially reduced flexibility of the chain atoms, (2) deviations from the spherical distribution of charge around the Ge atoms, *e.g.* due to ionized $Ge-O^-$ fragments, five-co-ordinated Ge atoms, *etc.*, and (3) rapid (on the n.m.r. time-scale) exchange between molecules of different structure.

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