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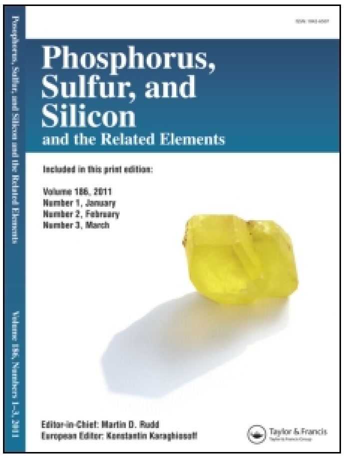

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THE INTERACTION OF BENZYL ALCOHOL WITH TRIMETHOXYBOROXINE : AMINE ADDUCTS OF TRIARYLBOROXINES AS MODEL COMPOUNDS

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The interaction of benzyl alcohol with trimethoxyboroxine has been investigated by hydrogen-1 and carbon-13 NMR and IR spectroscopy. These techniques indicate formation of a weak Lewis acid/base adduct, additionally stabilized by a hydrogen-bonding interaction, which undergoes rapid ligand exchange at room temperature. The system has been modelled by the synthesis and characterization of a series of amine-triarylboroxine adducts. These adducts rapidly undergo ligand dissociation-recombination in solution with ΔG^{+} of *ca.* 40-50 kJ/mol.

Keywords: Boroxines; Lewis base/acid adducts; Ligand exchange.

INTRODUCTION

Boron-containing Lewis acids such as $(MeO)_3B_3O_3$ (TMB) are able to initiate polymerization of epoxy resins[1] and epoxide monomers[2] and the 'pot-life' of the TMB/epoxy resin mixes can be been significantly increased by the inclusion of benzyl alcohol (BA) into the formulation[3]. The interaction of TMB with epoxides and the mechanism of polymerization is well documented[1]. However, little is known about the interaction of BA with TMB and ^{1}H, ^{11}B and ^{13}C NMR and IR spectroscopic results for this system are described herein.

RESULTS AND DISCUSSION

The proton and carbon-13 NMR spectra of of BA in $CDCl_3$ show changes upon addition of TMB consistent with (a) the formation of a labile adduct and (b) ligand exchange being fast at room temperature on the ^{1}H NMR timescale[4]. Thus, the signal observed for the methylene protons of BA are deshielded by 0.6 ppm relative to BA alone (4.4 ppm) with the new chemical shift similar to that for tri(benzyloxy)boroxine (5.2 ppm); the methylene carbon of BA is also deshielded by 0.9 ppm in the presence of TMB. Alkyloxy exchange does not appear to have occurred since signals due to free MeOH were not observed. Only one 'averaged' signal could be attributed to the methylene protons from a mixture with a higher BA:TMB ratio. Low temperature (-90°C) ^{1}H spectra of these samples revealed broadening of several peaks but were otherwise uninformative. $^{11}B\{^{1}H\}$ spectra were also broad and consistent with ligand exchange.

The TMB/BA system has been conveniently modelled by the use of amines and triarylboroxines ($Ar_3B_3O_3$)[5]. The reaction of stoichiometric quantities of amine and triarylboroxine in Et_2O at room temperature generally resulted in 1:1 adducts which were isolated as colourless air-stable crystalline solids[6]. Attempts to prepare BA complexes of triarylboroxines were unsuccessful. Similarly, reactions with PPh_3 or Et_2S with triarylboroxines did not give isolatable products. In solution the adducts undergo ligand exchange with free energies of activation (ΔG^+), as determined by variable temperature ^1H NMR spectroscopy, in the range 40-50 kJ/mol. This has been attributed to the process disrupting the delocalized boroxine π-system[7].

Several adducts of triarylboroxines have been characterized by single-crystal X-ray diffraction studies[7]. The structures of these adducts are characterized by alternating B_3O_3 six-membered rings, similar to the original boroxine ring system, with an additional co-ordinate bond from the amine nitrogen to one of the three ring boron atoms. The B-O ring distances involving the other two boron atoms are shorter on average than in the parent triarylboroxine and the internuclear distance is consistent with a localized stronger B-O π-interaction with the canonical form shown in Figure 1(a) having a significant contribution to the ground state structure.

IR spectra of BA (10%, vol) in C_6H_6, CH_2Cl_2, 40-60°C pet. ether, or $CHCl_3$ show changes consistent with the formation of additional hydrogen-bonds upon addition of TMB (30%, vol) *e.g.* in C_6H_6 solution the sharp 'free O-H' stretch (3,590 cm^{-1}) of BA disappears and the broad 'H-bonded O-H' stretch (3,410 cm^{-1}) grows in intensity and shifts to a lower wavenumber (3,220 cm^{-1}). The amine-triarylboroxine adducts described above do not display analogous H-bond absorptions in their IR spectra. Since the triarylboroxines do not possess *exo* oxygen atoms this allows us to speculate that the structure of the labile BA/TMB adduct is as shown in Figure 1(b) with the *exo* oxygen atom being implicated in the H-bonding interaction rather than an annular oxygen atom of the boroxine.

In conclusion, BA acts as an inhibitor for TMB initiated polymerizations of epoxy resins by competing with the epoxy resin oxirane oxygen atoms for the Lewis acidic TMB co-ordination sites. Co-ordination of BA onto one of the boron atom causes loss of Lewis acidity at this site and by a mesomeric effect also reduces the Lewis acidity at the other two boron sites. Alternatively, the H-bonded benzyl alcohol may sterically block the approach of the oxirane oxygen atoms to the boroxine ring.

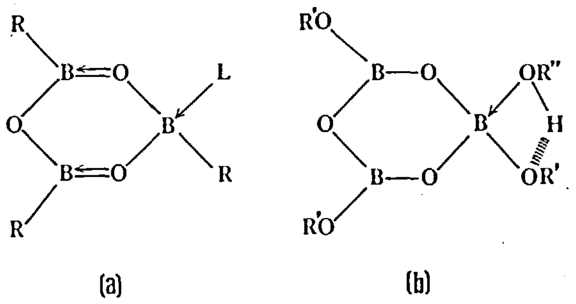

FIGURE 1 Schematic drawings of 1:1 Lewis base/boroxine adducts: (a) R = aryl, L = amine, and (b) R' = Me, R" = Bz.

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