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# FORMATION OF BOROXINE: ITS STABILITY AND THERMODYNAMIC PARAMETERS IN SOLUTION

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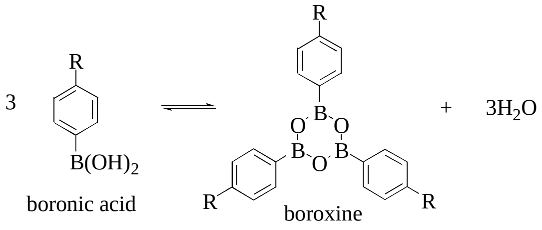
**Abstract -** Condensation of three boronic acids proceeding at room temperature gave their corresponding boroxines; NMR spectral measurements revealed that the reaction was reversible at room temperature, that electron-donating groups supported the formation of boroxine, and that entropically driven forces promoted the formation of boroxine in solution.

Boroxine, a cyclic anhydride of boronic acid, is a typical inorganic benzene. Experiments were performed to reveal the general nature of boroxine, including X-Ray analysis of structure,[1] MS spectroscopy to measure its stability in the gas phase,[2] characterization by vibrational analysis,[3] and calculations to identify polarizability or magnetizability.[3,4]

Boroxine is utilized in the material sciences. Tour *et al*.[5] reported its ability to act as a flame retardant when used as a polymer additive, and Mehta and Fujinami[6] showed its potential to enhance $Li^+$ transference number in polymer electrolytes. Boroxine is also of interest to organic chemists as an alternative compound to boronic acid for carrying out Miyaura-Suzuki coupling[7] and rhodium-catalyzed coupling;[8] its Lewis acidity has also been studied.[9] However, few papers[9] have discussed its properties in solution, even though hydrolysis of boroxine readily proceeds in the presence of water. We report here the formation and stability of triarylboroxine in solution and give details of the thermodynamic equilibrium between boronic acid and boroxine.

We chose several arylboroxines that possess electron-donating or -withdrawing groups at the *para*-position in the benzene ring and systematically analyzed their stability in the presence of water. The corresponding boronic acids were prepared using standard procedures[10] or commercially available versions were used. The reversible reaction between boronic acid and boroxine in the presence of water was clearly monitored by use of $^1$H NMR (500 MHz, $CDCl_3$).[11]

The equilibrium between boronic acid and boroxine



$$\boxed{K = \frac{[\text{boroxine}]\,[H_2O]^3}{[\text{boronic acid}]^3}}$$

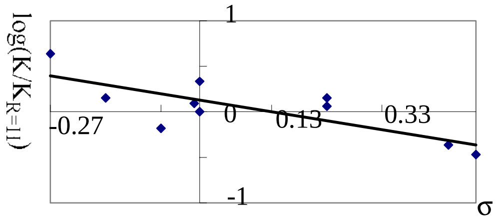
The equilibrium constants (K) at 25 °C were easily obtained, since integration showed the concentrations of these two compounds and water compared to that of the standard. The results are summarized in Table, and Hammett's plot for equilibria yielding straight line is shown in Figure. The results are as expected considering Hammett's plot for hydrolysis of *para*-substituted benzoates. Electron-withdrawing groups may accelerate the hydrolysis of boronic anhydrides; consequently, boroxine possessing electron-withdrawing substituents gave a small equilibrium constant. On the other hand, in the case of electron-donating substitutions, the equilibrium constant is larger, since electron-donating groups may reduce water reacting with boron atoms by nucleophilic displacement. In fact, the reverse reaction of electron-withdrawing boronic acid is faster than that of electron-donating boronic acid.

Next, NMR spectral experiments were performed at several temperatures to obtain thermodynamic information on the equilibria. The van't Hoff plots for all equilibria yield straight lines, and their thermodynamic parameters can be determined from the plots. The significant observation is that, in all cases, the formation of boroxine increases at a given temperature. The process involving construction of rigid boroxine would at first appear to be entropically unfavorable; however, it includes the release to the bulk solvent of three free water molecules from boronic acid. The formation of boroxine incurs an enthalpic cost, but this is counteracted by a larger entropy gain.

Table  Thermodynamic parameters of formation of a varietry of boroxines at 25°C

| R | K (mol/dm$^3$) | ΔG (kJ/mol) | σ | ΔH (kJ/mol) | ΔS (e.u.) |
|---|---|---|---|---|---|
| H | 0.32 | 2.82 | 0 | -14.3 | 0.0378 |
| OMe | 1.40 | -0.83 | -0.27 | -8.3 | 0.0305 |
| Me | 0.45 | 1.98 | -0.17 | -15.2 | 0.0419 |
| $SiMe_3$ | 0.21 | 3.87 | -0.07 | -17.7 | 0.0452 |
| Ph | 0.40 | 2.27 | -0.01 | -10.7 | 0.0287 |
| SMe | 0.69 | 0.92 | 0 | -10.3 | 0.0309 |
| Cl | 0.45 | 1.98 | 0.23 | -7.7 | 0.0187 |
| Br | 0.37 | 2.46 | 0.23 | -10.8 | 0.0278 |
| $CO_2Me$ | 0.14 | 4.87 | 0.45 | -14.5 | 0.0308 |
| COMe | 0.11 | 5.47 | 0.50 | -16.4 | 0.0355 |

Figure  Hammett's plot of data from Table



All experiments were performed more than twice, and the average is shown in Table. Concentration data were obtained from integrations of the appropriate signals for boronic acid , boroxine (total 3-19 mM), and water, compared with standard, hydroquinone dimethyl ether (19 mM), in the $^1$H NMR spectra recorded in $CDCl_3$.

Observation of *ortho*-substituted boronic acid gave additional insights. The equilibrium constant between *o*-methylphenylboronic acid and its boroxine has a smaller K value (0.28, 25 °C), than that of the corresponding *para*-substituted compound. This may be due to steric and stereoelectronic effects. The large size of the *ortho*-methyl group directly impedes the construction of boroxine. Due to the steric interaction of the methyl group, the three phenyl rings are twisted relative to the boroxine ring to give a propeller-like arrangement. This conformation results in a loss of electronic stability due to reduced overlap of the π-electrons in the benzene ring with the empty orbital of the boron atom. In fact, X-Ray crystallography has revealed the conformation of triphenylboroxine to be virtually planar.[1]

In conclusion, we confirm that the stability of arylboroxine depends on the properties of the electron environment of its aromatic groups, and that entropic driving forces result in the construction of boroxine in solution. In general, enthalpic gains promote the complexation of supramolecular structures, except for a few examples;[12] therefore, introduction of boroxine to supramolecular systems may produce a new type of molecular recognition.

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10. a) R = $CO_2Me$: B. Serafin and M. Makosza, *Tetrahedron*, 1963, **19**, 821; b) The boronic acid (R = TMS) was synthesized from known *p*-trimethylsiliylphenyllithium and trimethyl borate: J. M. Tour and E. B. Stephens, *J. Am. Chem. Soc*., 1991, **103**, 2309. R = TMS: IR$\nu_{max}$(KBr): 3400, 1350, 840, 645 cm$^{-1}$. $^1$H NMR (500 MHz, DMSO-$d_6$-$D_2O$ (10 : 1)) δ: 0.19 (9H, s), 7.41-7.48 (2H, m), 7.68-7.76 (2H, m).

11. Phenylboronic acid; $^1$H NMR (500 MHz, $CDCl_{3,}$ 25$^o$C) δ: 4.61 (1H, s), 7.39-7.44 (2H, m), 7.46-7.52 (1H, m), 7.72-7.75 (2H, m). Triphenylboroxine; $^1$H NMR (500 MHz, $CDCl_{3,}$ 25$^o$C) δ: 7.49-7.54 (2H, m), 7.58-7.63 (1H, m), 8.23-8.27 (2H, m).

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