

Kinetics and Mechanism of Hydrolysis of Boroxines

C. Li,^a L. Sotorrios,^b P. J. Boaler,^a A. M. R. Hall,^a V. Olikauskas,^a A. García-Domínguez,^a
A. G. Leach,^b G. C. Lloyd-Jones^{a,*}

^a School of Chemistry, University of Edinburgh, Edinburgh EH9 3FJ, U.K.

^b School of Health Sciences, The University of Manchester, Manchester M13 9PT, U.K.
c.li-99@sms.ed.ac.uk

The fundamental properties and applications of boroxines have been thoroughly researched,¹ and the reversibility of their formation have also been assessed from thermodynamic aspects.^{2,3} However, the kinetics and mechanism of boroxine formation and solvolysis are much less well understood because of the high reaction rates and water sensitivity. In this project, SF-UV and SF-NMR was used to monitor the hydrolysis, the kinetic roles of water were elucidated, and a Hammett analysis performed on substituted aryl boroxines. The reaction kinetics were then investigated in detail by NMR titrations, EXSY and magnetisation transfer experiments. The results show new features and pathways, in addition to the previously proposed mechanism.⁴ Direct degenerate exchange between the boroxine and boronic acid was identified, and further supported via exchange of hetero-boroxines. A new collection of mechanisms have been proposed to account for all of the observations.

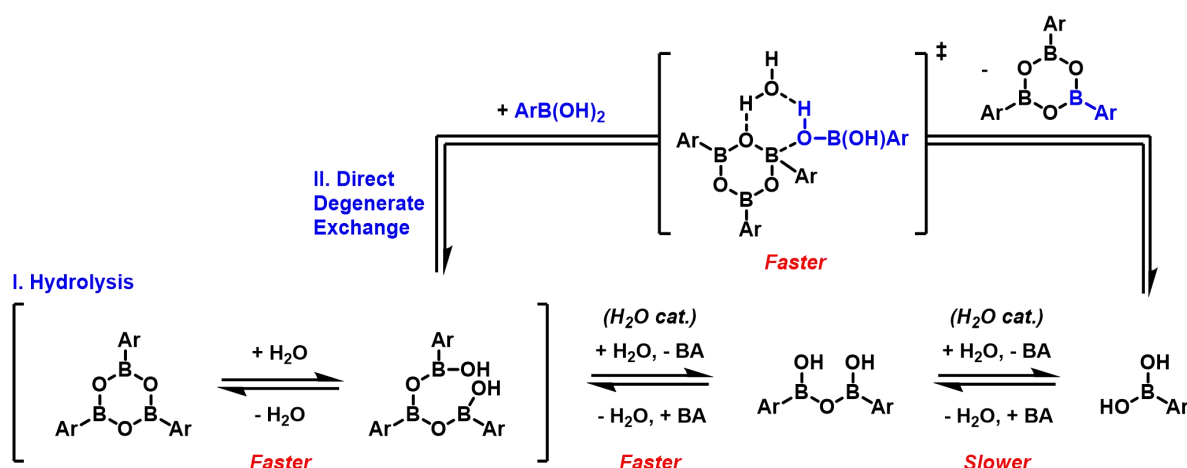


Figure 1. Proposed Mechanism of Boroxine Hydrolysis.

1 A. L. Korich, P. M. Iovine, *Dalton Trans.*, **2010**, 39, 1423-1431.

2 Y. Tokunaga, H. Ueno, Y. Shimomura, *et al.*, *Heterocycles*, **2002**, 57, 787.

3 a) J. Kua, C. R. Gyselbrecht, *J. Phys. Chem. A*, **2007**, 111, 4759-4766.; b) J. Kua, C. R. Gyselbrecht, *J. Phys. Chem. A*, **2008**, 112, 9128-9133.

4 K. G. Orrell, V. Šik, D. Stephenson, *Prog. Nucl. Magn. Reson. Spectrosc.*, **1990**, 22, 141-208.