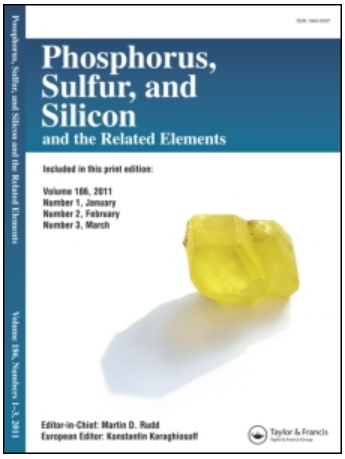

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Lewis Acidity in Haloalkyl Orthoborate and Metaborate Esters

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The Lewis acidities of a series of haloalkyl orthoborate and metaborate esters have been determined by Gutmann's ^{31}P NMR method. The introduction of halogens into the alkyl group of the borate generally increases the Lewis acidity at boron. Detailed analysis of data indicate that systematic variations correlate with Taft's electronic σ^* substituent parameters.

Keywords: Acceptor Number (AN); borate ester; haloalkyls; Lewis acid; Taft σ^* parameter

INTRODUCTION

Gutmann and co-workers[1] have described the Acceptor Number (AN) scale as a measure of Lewis acidity. This method conveniently makes use of the downfield shift, relative to that observed in hexane solution, of the ^{31}P NMR resonance of Et_3PO in Lewis acidic media. It has been previously shown that alkyl metaborate esters are strong

Lewis acids with AN values in the range 65-80, whilst alkyl orthoborate esters are weak Lewis acids with AN values in the range 12-25[2]. The effect of introducing halogen atoms into the alkyl chains has been investigated and is described in this report.

RESULTS AND DISCUSSION

Borate esters were prepared by reacting the haloalkyl alcohol with $B(OH)_3$ in toluene at reflux with removal of H_2O using a Dean-Stark apparatus, or by reaction of B_2O_3 with $B(OR)_3$ at ~200 °C in a sealed tube. All compounds were characterised by spectroscopic (IR and ^{11}B, ^{13}C, ^1H NMR) methods[3] and had satisfactory elemental analysis. Acceptor Numbers (AN) were obtained as previously described[2] for (a) $(RO)_3B$, R = ^nPr (**1**) 20.3; ^iPr (**2**) 21.6; $ClCH_2CH_2$ (**3**) 31.2; $ClCH_2CH_2CH_2$ (**4**) 33.9; $ClCH_2CH_2CH_2CH_2$ (**5**) 28.2; Cl_2CHCH_2 (**6**) 59.3; Cl_3CCH_2 (**7**) 71.5; $(ClCH_2)_2CH$ (**8**) 42.7; $BrCH_2CH_2$ (**9**) 38.1; ICH_2CH_2 (**10**) 45.6; F_3CCH_2 (**11**) 66.4; and (b) $(RO)_3B_3O_3$, R = Et (**12**) 80.1; ^nPr (**13**) 79.1, ^iPr (**14**) 73.5; ^nBu (**15**) 77.9; $ClCH_2CH_2$ (**16**) 79.4; $ClCH_2CH_2CH_2$ (**17**) 77.9; $ClCH_2CH_2CH_2CH_2$ (**18**) 77.4; Cl_2CHCH_2 (**19**) 80.5; Cl_3CCH_2 (**20**) 79.4; $(ClCH_2)_2CH$ (**21**) 79.4; F_3CCH_2 (**22**) 86.1. The esters **10** and **18-22** are previously unreported. Compounds **7** and **20** were waxy solids, and all others were liquids.

The alkyl orthoborate esters **1** and **2** had AN values which fell within the reported range[2] and the haloalkyl orthoborate esters **3-11** were stronger Lewis acids than related non-halogenated alkyl derivatives. The Lewis acidity of **11** was very high for an orthoborate ester and approached that more often observed in metaborate esters. The haloalkyl metaborate esters **16-22** were all moderately strong Lewis acids with AN values in the range 77.4-86.1. The haloalkyl metaborates were generally slightly more acidic than their related non-halogenated counterparts. Metaborate **22**, had a Lewis acidity

comparable to that of $B(C_6F_5)_3$ (AN = 82)[4] and BF_3 (AN = 89)[2].

Lewis acidity at boron is affected by electronic and steric factors with the electronic component being either inductive or mesomeric in origin. The haloalkyl esters described in this report are all derived from primary or secondary alcohols where it is anticipated that steric effects would be minimal. An increased Lewis acidity in borate esters derived from the sterically demanding trialkylsilyl alcohols has been attributed to mesomeric effects associated with the Si-O bond[5]. Taft[6] has correlated polar (inductive) effects for the alkoxy substituent of glycerate esters with their rate of hydrolysis. The Lewis acidity of borate esters may be similarly examined. A plot of Taft's σ^* substituent parameter[6] against the AN value of alkyl and haloalkyl orthoborate and metaborate esters is shown in Figure 1. The AN value for **15** (77.9) was remeasured for this study since the

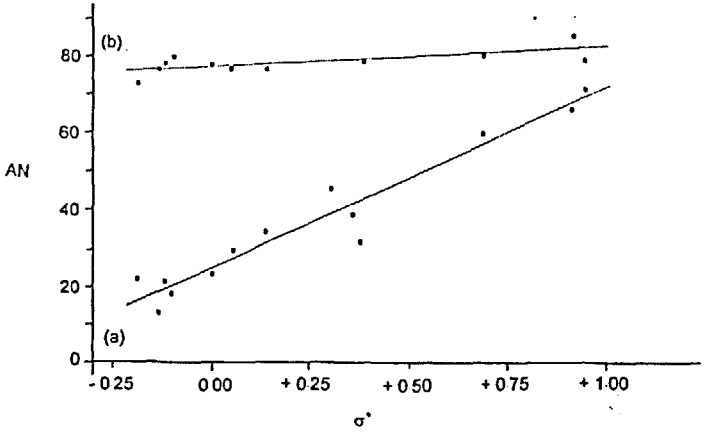

FIGURE 1 Plot of Taft's σ^* substituent parameter against AN value of (a) orthoborate and (b) metaborate esters with least-squares fit of AN = $(47.3 \pm 3.8)\sigma^* + (24.2 \pm 1.7)$ and AN = $(4.7 \pm 1.7)\sigma^* + (78.0 \pm 0.8)$, respectively. Data from *this work* and refs [2] and [6].

literature value (65)[12] appeared somewhat low and erroneous. There is a strong positive correlation (R = 0.97) for the orthoborates indicating that the σ^* term dominates the observed Lewis acidity of these compounds. A strong effect might be anticipated here since there is an alkoxide:boron ratio of 3:1. A positive trend is also apparent for the metaborate esters (R = 0.68) where the effect of the alkyl groups is moderated by the electronic effect of heterocyclic boroxine ring and the reduced alkoxide:boron ratio of 1:1.

To conclude, the relative Lewis acidities of orthoborate and metaborate esters have been shown to correlate with Taft's polar substituent parameters indicating that inductive effects associated with the alkyl and haloalkyl substituents are paramount in determining the Lewis acidities of these borate esters.

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