THE ELECTRONIC EFFECTS IN AND THE OXYGEN BASICITY OF SOME OXYGEN-CONTAINING BORANES

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Dedicated to Professor E. Hála on the occasion of his 60th birthday.

The oxygen relative basicity of di-n-butylboronous anhydride $((n\text{-}C_4H_9)_2B)_2O$, ethyl di-n-butylboronite $(n\text{-}C_4H_9)_2BOC_2H_5$ and some orthoborates $(RO)_3B$ having electrondonating and electronwithdrawing groups R was measured from the IR spectra of hydrogen bonds of phenol interacting with these compounds in CCl_4 and analysed by means of the Taft equation. The substituent electronic effect of $(n\text{-}C_4H_9)_2B$- and $(RO)_2B$-groups attached to the oxygen of the —OR and —OB= moieties has been estimated as a more electronwithdrawing than that of structurally alike R_2Z- and $(RO)_2Z$-groups having Z= CH and $SiCH_3$ and is discussed in terms of the vacant *2p* orbital of the boron and a weak, if any, mutual polarizability effect of the alkoxy groups in orthoborates. The trimethylsiloxy group in trimethylsilyl borate possesses reduced electronwithdrawing ability compared to that in $((CH_3)_3SiO)_3SiCH_3$ as a consequence of its great polarizability.

The literature contains numerous contributions[1-4] to physical properties of the organoboron compounds with the B—O bond(s). Much is yet, however, to be discovered about the substituent electronic effect of the R_2B- and $(RO)_2B$-groups and the RO-groups interaction in $R_nB(OR)_{3-n}$ compounds.

Published results on similar systems like ethers[5], alkoxysilanes[6-9] and siloxanes[10] indicate the substituent electronic effect parameter of the groups attached to the oxygen as easily available from the IR spectra of hydrogen bonds of phenol interacting with the oxygen of these compounds in CCl_4. Using this simple IR technique for the determination of the proton-accepting ability of the oxygen in orthoborates $(RO_3)B$, di-n-butylboronous anhydride $((n\text{-}C_4H_9)_2B)_2O$, and ethyl di-n-butylboronite $(n\text{-}C_4H_9)_2BOC_2H_5$ we have attempted in this note to estimate the substituent electronic effect of R_2B- and $(RO)_2B$-groups attached to the oxygen of the —OR and —OB= moieties and to assess the role of the mutual polarizability effect (MPE) of the RO-groups on the boron atom. The MPE is of a great importance[8,11] in organosilicon compounds $(RO)_nSiR_{4-n}$ and its appraisal in orthoborates $(RO)_3B$ seems worthy, since orthoborates serve as a proper model to ellucidate the role of the M—O bond polarity in controlling the MPE of the RO-groups in the $(RO)_xMR_y$ system.

EXPERIMENTAL

Model compounds. All the orthoborates were, unless otherwise noticed, prepared by the reported[1] treatment of either boron trichloride[1] or sodium borohydride[12] with appropriate alcohols. Trimethylsilyl[13] and triphenyl[14] borate were obtained by a reaction of orthoboric acid with trimethylchlorosilane and phenol, respectively. Di-n-butylboronous anhydride was prepared[15] by a treatment of aqueous hydrobromic acid with tri-n-butylboron and ethyl di-n-butylboronite[16] was obtained by reaction of di-n-butylboronous anhydride with ethanol. The compounds were, after rectification under nitrogen, checked for purity by gas-liquid chromatography and elemental analysis.

Relative oxygen basicity of oxygen-containing boranes was determined from the IR spectra of hydrogen bonds of phenol interacting with these compounds in CCl_4. The IR spectra were recorded on a double-beam Zeiss (Jena) spectrometer, Model UR 20 using 1 mm thick KBr cells. Protondonating phenol was used in 0·02M concentration and the oxygen-containing boranes (proton acceptors) as 0·1 – 1·0M solutions in spectrograde CCl_4. In studying the dependence of the proton-acceptor concentration on the absorption band pattern of the hydrogen bond with orthoborates having $R = t\text{-}C_4H_9$, $n\text{-}C_4H_9$, $(CH_3)_3Si$, Cl_3CCH_2, $HC\equiv CCH_2$ and C_6H_5 we have found that the occurrence of the $\nu_{(OH)}^{assoc.}$ band for $R = t\text{-}C_4H_9$ is observed with the least concentration (0·1M). At higher $(t\text{-}C_4H_9O)_3B$ concentrations the $\nu_{(OH)}^{assoc}$ band disappeared. Such an effect was not met with the sterically analogous $((CH_3)_3SiO)_3B$ compound. In common, the $\nu_{(OH)}^{assoc}$ bands are of a low intensity and a considerable half-width (this is especially true with chloroalkyl, tert-butyl and trimethylsilyl orthoborates), which decrease the accuracy of the $\Delta\nu(OH)$ value determination below $\pm 3\ cm^{-1}$. The other protonaccepting center X in R (π-bonds in C_6H_5, $CH_2{=}CHCH_2$, $HC\equiv CCH_2$ or chlorine in chloroalkyl) form the $\nu(OH)^{assoc}$ band ($\Delta\nu(OH) = 20 - 60\ cm^{-1}$) that does not interfere with the band belonging to the $\nu_{OH...O}$ vibration. However, the concentration increase of a protonacceptor results in a pronounced intensity of the $\nu_{OH...X}^{assoc}$ band, the intensity of the $\nu_{OH...O}^{assoc}$ band remaining about unchanged. This fact put also some constraint on the protonacceptor concentration used.

RESULTS AND DISCUSSION

In discussing the oxygen proton-accepting ability ($\Delta\nu(OH)$) of the oxygen containing boranes we make use of its comparison with the $\Delta\nu(OH)$ value of structurally similar oxygen-containing alkanes and silanes. While the oxygen basicity of the former $(CH_3)_nC(OC_2H_5)_{4-n}$ compounds appears in harmony with the substituent parameter $\sigma^*_{C_2H_5O}$, that of the ethoxysilanes $(CH_3)_nSi(OC_2H_5)_{4-n}$ reflects the reduced $-I$ effect of the ethoxy groups[8]. This reduction has been shown to result from the operation of the MPE of the ethoxy groups and was ascribed to an easier polarizability of the Si—O bond[8]. Both the silicon and boron atoms possess low-lying vacant ($2p$ or $3d$) orbital(s) enabling the B—O and Si—O bond to have sufficient double-bond character. While our $\Delta\nu(OH)$ data on the polyalkoxysilanes $(CH_3)_nSi(OR)_{4-n}$ with n = 0 – 2 indicate[8,11,17] that the double-bond character is extinguished in these compounds, this character is suggested[1-3] to survive in orthoborates $(RO)_3B$. This might indicate that a higher electropositivity of the atom M in a MO_x moiety can be a stimulating force for the $O \rightleftarrows M$ back-bonding, and chiefly, that rather $2p$ than $3d$ orbitals are suitable for the overlap with the n orbitals of the oxygen. Herein measured oxygen basicity of some oxygen-containing boranes in CCl_4 using phenol as a reference acid (Table I and the data below) can be consulted on this point.

Let the electronic effect of dialkylboryl group attached to the —OR and —OBR_2 moiety be discussed first on the basis of the oxygen basicity ($\Delta\nu$(OH) in cm^{-1}) of structurally similar etheral compounds of carbon, silicon and boron. As for the etheral oxygen linked to the same types of the atom, its basicity decreases from the carbon *via* the silicon to the boron compounds:

	dialkyl ethers	hexaalkyldisiloxanes	$((n\text{-}C_4H_9)_2B)_2O$
$\Delta\nu$(OH):	275 ± 10 (res[5,18])	170 ± 10 (ref.[19])	90 ± 10

The most electronwithdrawing ability of dialkylboryl (the di-n-butylboryl) group is also seen with compounds in which alkyl (the n-butyl), trialkylsilyl (the trimethylsilyl), and dialkylboryl (the di-n-butylboryl) groups are bonded to the —OC_2H_5 moiety:

	$n\text{-}C_4H_9$—OC_2H_5	$(CH_3)_3Si$—OC_2H_5	$(n\text{-}C_4H_9)_2B$—OC_2H_5
$\Delta\nu$(OH):	277 (ref.[18])	271 (ref.[20])	221 ± 3

In view of 1) the earlier proposed electronic effect composition[21] (a blend of the polar

TABLE I

Wavenumber Shift, $\Delta\nu$(OH) in cm^{-1}, of Phenol Due to Its Interaction with $(RO)_3B$ in CCl_4 and Parameter σ^* of $(RO)_2B$-Groups in These Compounds

R	$\Delta\nu$(OH)[a]	$\sigma^*_{(RO)_2B-}$[b]
$(CH_3)_3C$	245	0·35 ± 0·08
$(CH_3)_2CH$	222	0·53 ± 0·08
$n\text{-}C_4H_9$	212	—
C_2H_5	214	0·50 ± 0·06
CH_3	189	0·62 ± 0·08
$Cl(CH_2)_3$	173	—
$CH_2{=}CHCH_2$	181	0·68 ± 0·07
$Cl(CH_2)_2$	148	0·75 ± 0·08
$HC{\equiv}CCH_2$	154	0·70 ± 0·10
C_6H_5	114	—
Cl_3CCH_2	115	—
$(CH_3)_3Si$	200	0·71 ± 0·06

[a] Experimental error 3—8 cm^{-1}. [b] Obtained from the $\Delta\nu$(OH) of the orthoborates and the $\Delta\nu$(OH) *vs* $\sigma^*_{(X)}$ plot for X—O—R compounds[5].

and the polarizability effect of a substituent), and 2) the suggestion[5,7] that the resultant electron density on the ethereal oxygen is controlled by a mutual operation of the polar effect of one and the polarizability effect of the second substituent, both the effects being opposed to each other (*i.e.* the polar effect contribution to the electron density at the oxygen in R—O—R′ by R is attenuated by the polarizability effect of R′), the above basicity orderings indicate high electronaccepting ability and low polarizability effect of the di-n-butylboryl group in the above compounds.

To explain the low oxygen basicity of the oxygen linked to the boron atom, the $n_0 \rightarrow p_B$ electron orbitals overlap has to be undoubtedly considered, since the higher electropositivity of the boron should contrarily lead to a relatively higher $\Delta\nu(OH)$ value in the B—O compound(s). The electronic effect parameter σ^* for the di-n-butylboryl group 0·43 ± 0·06 obtained from the $\Delta\nu(OH)$ value of $(n\text{-}C_4H_9)_2B—OC_2H_5$ and the $\Delta\nu(OH)$ *vs* $\sigma_X^{(*)}$ plot for the $X—OC_2H_5$ compounds[5] confirms this observation.*

In passing now from the monooxygensubstituted boranes to orthoborates $(RO)_3B$, their oxygen basicity decreases with the increasing $-I$ effect of the group R (Table I). The electronic effect of the $(RO)_2B$-groups in $(RO)_3B$, *i.e.* the electronic effect of the $(RO)_2B$-groups attached to the —OR moiety can be easily estimated on the basis of the linear relationship $\Delta\nu(OH)$ *vs* $\sigma^*_{(X)}$ for individual X—OR sets differing in R (ref.[5]) and from the $\Delta\nu(OH)$ values of the $(RO)_2B—OR$ orthoborates. The $\sigma^*_{(RO)_2B-}$ parameters obtained are given in Table I and show 1) all the $(RO)_2B$ groups attached to the oxygen of the —OR moiety to operate as electronwithdrawing groups,

TABLE II

Wavenumber Shift, $\Delta\nu(OH)$ in cm^{-1}, of Phenol Due to Its Interaction with $(RO)_3Z$ in CCl_4 and σ^* Parameter of $(RO)_2Z$— Groups in These Compounds

R	$\sigma^*_{(RO)_2Z-}$	
	Z = $SiCH_3$[a]	Z = B
C_2H_5	0·27 ± 0·05	0·50 ± 0·08
CH_3	0·28 ± 0·05	0·62 ± 0·08
$CH_2{=}CHCH_2$	0·39 ± 0·05	0·68 ± 0·07
$Cl(CH_2)_2$	0·42 ± 0·06	0·75 ± 0·08
$HC{\equiv}CCH_2$	0·55 ± 0·08	0·70 ± 0·10

[a] Ref.[22].

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* The electronic effect parameter σ^* for alkyl (0—(−0·3) and trialkylsilyl (−0·15— (−0·27), ref.[22]) attached to the $—OC_2H_5$ moiety is lower.

and 2) their electronwithdrawing action to be pronounced with the more electronwithdrawing R.

Table II gives comparison of the σ^* electronic effect parameters of the $(RO)_2CH_3.$ .Si- and $(RO)_2B$-groups. There appears plausible to state that generally higher σ^* parameter of the dialkoxyboryl groups indicates a less marked, if any, MPE of the alkoxy groups attached to the boron atom. This interpretation of the oxygen basicity of the orthoborates is consonant with the $\Delta\nu(OH)$ values gathered in Table III, wherein the oxygen basicity of structurally similar $(C_2H_5O)_3Z$ compounds with $Z = SiCH_3$, CCH_3 and B is compared. The oxygen basicity of the orthoborates and the substituent $\sigma^*_{(C_2H_5O)_2B-}$ parameter are much closer to the basicity and the $\sigma^*_{(C_2H_5O)_2Z-}$ parameter of the carbon than the silicon compounds. Indeed, the oxygen basicity of the orthoborates looks then as not controlled by the MPE since, as mentioned above, the MPE does not operate in the carbon but in the silicon compounds. The MPE in MO_x moiety thus does seem to be favored with decreasing σ—M—O bond polarity.

The conclusion on the relative weakness or the absence of the MPE operation in various $(RO)_3B$ systems (Table I) does not, however, appears to rule out the possibility of the MPE operation in some more special $(RO)_3B$ systems. The comparison of the oxygen basicity in trimethylsilyl orthoborate with that of the structurally similar silane $((CH_3)_3SiO)_3SiCH_3$, and the comparison of the σ^* parameters of $((CH_3)_3SiO)_2CH_3Si$- and $((CH_3)_3SiO)_2B$-groups (Table IV) reveals the oxygen basicity of the orthoborate to be higher and the electronwithdrawing action of bis(trimethylsiloxy)boryl group to be lower. Apparently, the importance of the MPE of the trimethylsiloxy groups on the boron mounts over that on the silicon. The electronwithdrawing ability of $(CH_3)_3SiO$-group in the orthoborate has to be dramatically reduced. Similar variation of the electronic effect of silyl groups has already been encountered with when passing from the silyl —OC_2H_5 to the silyl —OCH_2CCl_3

TABLE III

Wavenumber Shift, $\Delta\nu(OH)$ in cm^{-1}, of Phenol Due of Its Interaction with $(C_2H_5O)_3Z$ in CCl_4 and Parameter σ^* of $(C_2H_5O)_2Z$-Groups in These Compounds

Z	$\Delta\nu(OH)$	$\sigma^*_{(C_2H_5O)_2Z-}$ [b]
$SiCH_3$	237[a]	0·27 ± 0·05
B	214	0·50 ± 0·06
CCH_3	201[a]	0·62 ± 0·06

[a] Ref.[20]. [b] Obtained from the $\Delta\nu(OH)$ of $(C_2H_5O)_3Z$ and the plot of the $\Delta\nu(OH)$ *vs* $\sigma^*_{(X)}$ for $X\text{-}OC_2H_5$ (ref.[5]).

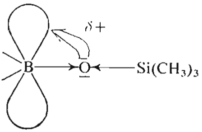
system[6,7]. In that case the strongly electronwithdrawing Cl_3CCH_2-group was supposed to develop electron deficiency on the oxygen which was further diminished by otherwise electronwithdrawing silyl group as a consequence of its great polarizability. Here presented reduction of $-I$ effect of $(CH_3)_3SiO$-group in the orthoborate is, more probably, caused by the competition of the vacant $2p$ and $3d$ orbitals of the boron and silicon for the n electrons of the oxygen. The resulting electron deficit might then be decreased due to the high polarizability of the σ—O—Si bond (structure *I*), or from the diminishing (extinguishing) of the $(p-d)_\pi$ overlap (structure *II*).

TABLE IV

The Oxygen Basicity, $\Delta\nu(OH)$ in cm^{-1}, of $((CH_3)_3SiO)_3Z$ and the σ^* Electronic Effect Parameter[a] of $(CH_3)_3SiO)_2Z$-Groups in These Compounds

Z	$\Delta\nu(OH)$	$\sigma^*_{[(CH_3)_3SiO]_2Z-}$
$SiCH_3$	136[b]	1·37 ± 0·10
B	200	0·71 ± 0·06

[a] Parameter σ^* obtained from the $\Delta\nu(OH)$ of $((CH_3)_3SiO)_3Z$ and the $\Delta\nu(OH)$ *vs* $\sigma^*_{(X)}$ plot for X-$OSi(CH_3)_3$ (ref.[23]). [b] Ref.[10].



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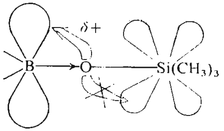

II

The trimethylsilyl orthoborate thus serves as a further system documenting an enormous polarizability of the Si—O bond and an easy electronic effect variation of electronwithdrawing silyl groups.

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