^{1}H NMR STUDY OF HYDROGEN BONDING OF FLUORINATED ALCOHOLS WITH ETHERS

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Summary: The hydrogen bonding of TFE and HFIP with t-BuOCH$_3$ (1) and PhOCH$_3$ (2) was studied using ^{1}H NMR. The $\Delta\delta$ values of carbon-bound hydrogens in 1 and 2 show good linear correlation with the alcohol acidity.

Alcohols containing one or more perfluoroalkyl groups attached to the α-
-carbon are more acidic[1,2] than the corresponding fluorine-free alcohols, and
consequently they are extremely strong hydrogen-bonding donors which can form
complexes with various bases.[2] Among several methods used in investigation of
such intermolecular hydrogen bonding, the NMR technique was shown to be very
useful.[2-7] However, in these spectroscopic studies only the ^{1}H NMR shifts of
a hydroxyl group[2,3] (or NH group[4]) in hydrogen-bonding complexes were meas-
ured, or in very few cases ^{13}C NMR[5], ^{15}N NMR[6], and ^{19}F NMR[7] data of such com-
plexes were collected.

In continuation to our interest[8] in fluorinated alcohols as solvolytic
solvents,we investigated the intermolecular hydrogen bonding of 2,2,2-tri-
fluoroethanol (TFE) and 1,1,1,3,3,3-hexafluoro-2-propanol (HFIP), as well as
of their non-fluorinated analogues i-PrOH and EtOH with t-BuOCH$_3$ (1) as pro-
ton acceptor (Figure 1). These interactions were studied using ^{1}H NMR for
measurement of the chemical shifts of carbon-bound hydrogens in the ether part
of the complex and not as usual of the OH group. The ^{1}H NMR signals of ether
1 in these complexes show downfield shifts relative to the reference signals
of the same ether in CCl$_4$ solution without the presence of a hydrogen-bonding
donor. These shifts of ^{1}H NMR signals are measured at room temperature and
defined as $\Delta\delta$ values. Their magnitude (at certain temperature) depends on the
type of C-H bond in ether, on the structure of alcohol, and on the molar ra-
tio alcohol-ether. The change of $\Delta\delta$ value with concentration of alcohol is
most pronounced with HFIP (which is the strongest acid[2] among the studied al-
cohols), less pronounced with TFE[1], whereas with EtOH and i-PrOH (which are
weaker acids[1,9]) much smaller dependence of $\Delta\delta$ values on the concentration of
alcohol was obtained. The presented curves show drastic change of $\Delta\delta$ values
for all investigated alcohols with the molar ratio alcohol-ether being smaller
than 2-3, and with further increase of this ratio the change in $\Delta\delta$ values is

(a) $(CH_3)_3C-O-\underline{CH}_3$

$\Delta\delta$(Hz)

(b) $(C\underline{H}_3)_3C-O-CH_3$
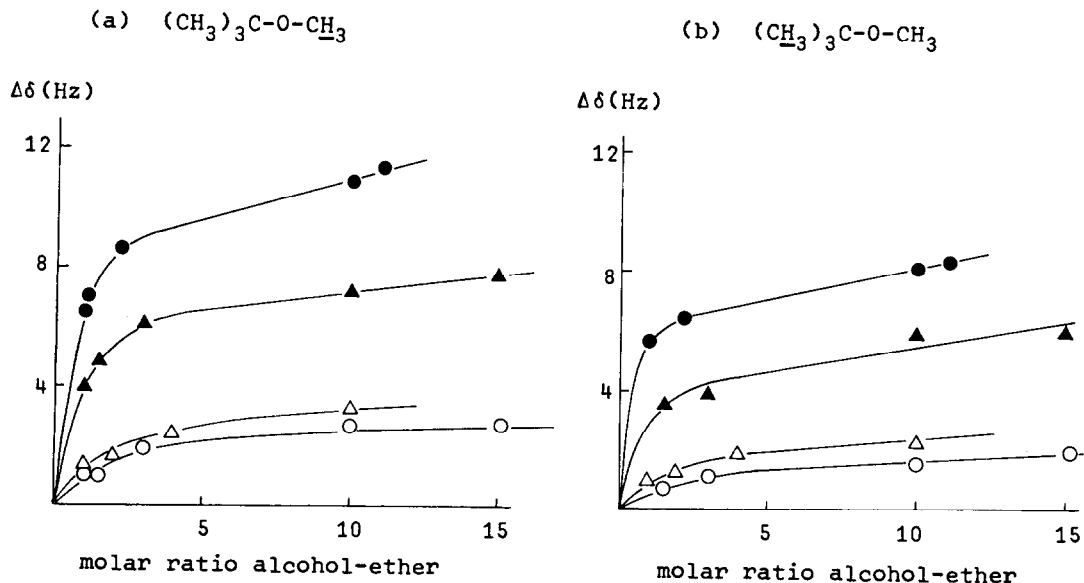
$\Delta\delta$(Hz)

Figure 1. The $\Delta\delta$ values for (a) MeO group, and (b) t-BuO group of ether 1 in complexes with HFIP (●), TFE (▲), i-PrOH (○), and EtOH (△), in dependence of concentration of these alcohols.

not so pronounced. The $\Delta\delta$ values of studied complexes (measured at the molar ratio alcohol-ether 10:1) show good correlation (correlation coefficients are about 0.997) with the pK_a values of alcohols. A similar behavior was observed for other studied ethers such as $PhOCH_3$ (2).

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