THE POLARIZABILITY OF SOME GROUPS ATTACHED TO OXYGEN IN ETHERS

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Relative basicity of the oxygen in ethers R—O—R′, $\Delta\nu(OH)$, was measured from the IR spectra of hydrogen bonds of phenol interacting with R—O—R′ in CCl_4 and is shown to be controlled by a blend of polar and polarizability effect of R and R′ groups. Linear regression analysis of the $\Delta\nu(OH) - \sigma^*_{(R)}$ and $\Delta\nu(OH)$ — percentage s character of $C(\beta)$—$C(\gamma)$ bond in R for individual series of R—O—R′ with R′ = alkyl groups, H, H_2C=$CHCH_2$, $C_6H_5CH_2$, $Cl(CH_2)_2$, $HC\equiv\equiv CCH_2$, C_6H_5 and $ClCH_2$ yield the scale of polarizability effect of R′ groups. Mechanism of polarizability effect in ethers is discussed.

The electronic effect of a substituent is suggested to result from seven different modes of interaction between a substituent and position of its attachment[1]. The additional types of the interaction can arise when a probe is introduced[1]. The success of dual--substituent parameter (DSP) approach suggests however the electronic effect of a substituent as deriving from two factors, one describing its polar nature and one its tendency to undergo charge-transfer with adjacent orbital of π symmetry[1,2]. In the gas phase or a medium of low polarity, where no solvation effects[3−5] operate, the electronic effect of a substituent, being suggested as a blend of polar and polariz-ability[6−8] effects, can be compounded only by conformational[9] effects. The estima-tion of electronic substituent parameter, or a scale of them, in such media is there-fore most worth-doing[10].

Properties of substituted aliphatic derivatives in low polar media have been reported to follow the σ_I values of the substituents[2]. On the other hand, it was shown in many cases that such properties can be well fitted by DSP equation with a significant resonance term[2]. Both the polarizability and conformational effects do not likely offer major contributions to the measured substituent effect in these instances.

Complexation between a proton-accepting atom of solute and a suitable proton donor in an excess of hydrocarbon or CCl_4 appears to be affected by solvation phenomena only slightly. With a view to attempt to estimate the role of polari-zability effect of groups bonded to oxygen, we present in this note an analysis of the oxygen basicity of ethers measured by IR spectroscopy in CCl_4.

EXPERIMENTAL

All ethers, the IR basicity of which was measured in this work, were prepared by usual procedures described in literature. Their purity was checked by gas–liquid chromatography and the identity was confirmed by NMR spectroscopy or elemental analysis. All the t-butyl ethers were obtained by the addition of corresponding alcohols to isobutene catalysed by sulfonated polystyrene cross-linked with divinylbenzene "Ostion KSP" (supplied by Spolek pro chemickou a hutní výrobu, Ústí n. L.). The reaction was carried out in autoclave (70°C, 3 h) and produced the t-butyl ethers in 35–45% yields. Three ethers have been prepared for the first time: both 2-propargyloxy-1-chloroethane (b.p. 148·5°C, n_D^{20} 1·4520, 82% yield) and 2-cyclohexyloxy-1-chloroethane (b.p. 205°C, n_D^{20} 1·4637, 40% yield) have been obtained by a treatment of 2-chloroethanol with sodium in propargyl alcohol and cyclohexanol respectively, yielding 2-propargyloxyethanol (b.p. 176°C, n_D^{20} 1·4502, 42% yield), and 2-cyclohexyloxyethanol (b.p. 157°C/140 Torr, 21% yield), and by following reaction of these compounds with thionyl chloride in ether. Propargyloxycyclohexane (b.p. 158°C, n_D^{20} 1·4630) was prepared by a treatment of propargyl bromide with sodium cyclohexanolate in ether. The oxygen relative basicity of ethers was determined from the IR spectra of hydrogen bonds of phenol due to interaction with ethers. The IR spectra were recorded in the region of LiF prism (NaCl cells of 0·1 cm thickness) with a double beam Zeiss, Model UR-20, spectrophotometer. The concentration of phenol and ethers in pure CCl_4 was 0·02 and 0·1–0·2M, respectively. The experimental conditions of the oxygen basicity measurements of alcohols were identical with those described elsewhere[11]. Wavenumbers of absorption band maxima were obtained as an average of three measurements.

RESULTS AND DISCUSSION

The IR spectroscopic determination of basicities[12] in aprotic CCl_4 is based on the Badger–Bauer relationship[13,14], whose general applicability for appropriately chosen systems was confirmed[15-17]. The IR absorption spectra of hydrogen bonds of phenol interacting with alcohols or ethers in CCl_4 have been shown to reflect proton acceptor ability of alcoholic or etheral oxygen[12,18,19]. The solvation effects in highly diluted solutions of phenol and oxygen-containing solute in CCl_4 should be of slight importance[20,21].*

The influencing of equilibrium (A) by solvent consists only in formation of collision complexes[22] of all the components present. Hence, an information on the electronic effect of substituents bonded to the oxygen can be acquired.

There are a few papers dealing with the correlation between the basicity of the oxygen (in alcohols[11,19], ethers[18,19] and alkoxysilanes[24]) and the parameter of the polar effect of groups attached to the oxygen. As to ethers R—O—R′, the correla-

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*   Comparison of gas-phase strengths with hydrogen-bond formation with *p*-fluorophenol in CCl_4 reflects that no relationship between these two quantities exists in general (comprising different species, such as amines, anilines, carboxylic acid amides and esters, ethers, ketones, *etc.*)[8]. Very little resemblance between these two quantities primarily results obviously from specific solvent–solute interaction which was considered in CCl_4 for nitrogen bases[23], and can intensify steric effect of a substituent in base.

tion $\Delta\nu(OH)$ vs $\sum\sigma^*_{R,R'}$ reported[18] reflects the authors' effort to put all $\Delta\nu(OH)$ values on one correlation line. The electronic effect, that is a blend of polar and polarizability effects, of a substituent bonded to the oxygen can then be considered constant regardless a moiety to which the substituent is attached.

$$[R—O—R']_{CCl_4} + [PhOH]_{CCl_4} \rightleftharpoons \left[R—O\begin{matrix} ^{\cdots H^{\cdots OPh}} \\ R' \end{matrix} \right]_{CCl_4} \qquad (A)$$

Our analysis of the $\Delta\nu(OH)$ data on ethers (Table I) shows that $\Delta\nu(OH)$ data are well fitted by the correlation equation (2) separately treating the individual series

TABLE I

$\Delta\nu(OH)$ Data for ROR'

R'	R, $\Delta\nu(OH)^a$
t-Bu	t-Bu[b], 321; i-Pr[b], 305; n-Pr, 301; Et[b], 296; Me[b], 295; H[c], 243; CH_2=CHCH$_2$, 276; PhCH$_2$, 256; Cl(CH$_2$)$_2$, 254; HCl$_2$CCH$_2$, 221; HC≡CCH$_2$, 232; Cl$_3$CCH$_2$, 131.
i-Pr	i-Pr[b], 293; Et[b], 287; Et[b], 227; H[c], 238; CH_2=CHCH$_2$, 262; PhCH$_2$, 269; Cl(CH$_2$)$_2$, 238; HC≡CCH$_2$, 226; ClCH$_2$, 153.
c-Hex	t-Bu, 311; Me, 281; H[d], 242; CH_2=CHCH$_2$, 272; Cl(CH$_2$)$_2$, 242; HC≡CCH$_2$, 231; ClCH$_2$, 164.
Et	n-Bu[b], 277; n-Pr[b], 272; Et[b], 271; H[c], 227; CH_2=CHCH$_2$[b], 256; Cl(CH$_2$)$_2$[b], 227; HC≡CCH$_2$, 215; ClCH$_2$[b], 145.
Me	n-Bu[b], 263; n-Pr[b], 263; Me[b], 246; H[c], 215; CH_2=CHCH$_2$[b], 241; PhCH$_2$, 244; Cl(CH$_2$)$_2$[b], 208; HC≡CCH$_2$, 205; ClCH$_2$, 132.
H_2C=CCH$_2$	H[c], 205; CH_2=CHCH$_2$[b], 237; PhCH$_2$, 234; Cl(CH$_2$)$_2$, 209; HC≡CCH$_2$, 201; ClCH$_2$, 133.
PhCH$_2$	n-Pr, 257; H[c] 213; PhCH$_2$[e], 233; Cl(CH$_2$)$_2$, 206; HC≡CCH$_2$, 201.
Cl(CH$_2$)$_2$	n-Pr, 230; H[c], 189; Cl(CH$_2$)$_2$[b], 178; HC≡CCH$_2$, 170; CF$_3$CH$_2$, 120; ClCH$_2$[b], 117.
Ph	n-Bu[b], 164; n-Pr, 164; Et[b], 165; Me[b], 157; H[c], 130; CH_2=CHCH$_2$[b], 150; Br(CH$_2$)$_2$, 134; HC≡CCH$_2$[b], 124.
CH_2=CH[b]	t-Bu, 183; i-Pr, 169; n-Bu, 160; n-Pr, 155; Et, 155; Cl(CH$_2$)$_2$, 120; Br(CH$_2$)$_2$, 118; I(CH$_2$)$_2$, 123; F(CH$_2$)$_2$, 117.
HC≡CCH$_2$	n-Bu[b], 208; n-Pr, 215; H, 170; HC≡CCH$_2$, 167;
ClCH$_2$	ClCH$_2$, 109.
H[c]	n-Pr, 228; Br(CH$_2$)$_2$, 199; Cl$_2$CHCH$_2$, 155; Cl$_3$CCH$_2$, 124.

^{a} In cm^{-1}, ^{b} ref.[18]; ^{c} ref.[11]; ^{d} ref.[19]; ^{e} ref.[25].

of R—O—R' with R' = t-C_4H_9, i-C_3H_7, c-C_6H_{11}, C_2H_5, CH_3, $C_6H_5CH_2$, CH_2=
=$CHCH_2$, $Cl(CH_2)_2$, $HC \equiv CCH_2$, $HC = CH_2$, C_6H_5, $ClCH_2$ and H (Table II),

$$\Delta v(OH) = \varrho^* \cdot \sigma^*_{(R)} + C \qquad (1)$$

provided that no $\Delta v(OH)$ data for R—O—R' with R conjugating with the oxygen
(as C_6H_5, $CH_2=CH$) are included into the correlation. The slopes (ϱ^* constants)
of the individual $\Delta v(OH)$ vs $\sigma^*_{(R)}$ plots differ and perusal of Table II reveals that while
the ϱ^*'s of alkyl groups are comparable in magnitude excepting that for t-C_4H_9,
those for the other R' decrease with decreasing electron-donating ability of R'.
Similarly, the oxygen basicity decrease in the sequence $CH_3CH_2CH_2OR'$, CH_2=
=$CHCH_2OR'$, $CH \equiv CCH_2OR'$ is essentially linear with the percentage s character
of $C(\beta)$—$C(\gamma)$ bond (%s), and linear regression analysis of the $\Delta v(OH) - (\%s)$ rela-
tionship indicates different slopes for the individual series ROR' having different R':
t-C_4H_9 (2·74 ± 0·08) > i-C_3H_7 (2·34 ± 0·24) ~ C_2H_5 (2·45 ± 0·14) ~ CH_3 (2·30 ±
± 0·12) ~ $Cl(CH_2)_2$ (2·39 ± 0·06) ~ H (2·29 ± 0·12) ~ $C_6H_5CH_2$ (2·20 ± 0·21) >
> $HC \equiv CCH_2$ (2·94 ± 0·08) > C_6H_5 (1·59 ± 0·06). The experimental conditions
of the IR spectral measurement of $\Delta v(OH)$ make one assure that the different slopes
have to reflect different polarizability effect of R' groups. Hence, the polar contribu-
tion to the substituent electronic effect of R and R' groups has to be compounded
by polarizability effect of these groups. (If not, an identical slope of both the above
relationships should have been obtained).

Polarizability effect is believed to operate in a direction to favor a molecular
center with electronic excess or deficit and is considered to be proportional in magni-
tude to an extent of the electronic excess or lack on a center to be stabilized. Polariz-
ability effect of R' should then diminish the oxygen basicity when R are electron-
supplying, and, *vice versa*, increase it when R are electron-withdrawing. Considering
the Taft σ^* constants to be valid measures of the polar effect of substituents in CCl_4,*
polarizability effect of R' in R—O—R' can be conceived to operate as in structures *I*
and *II* and its consequence in the $\Delta v(OH)$ vs $\sigma^*_{(R)}$ plot can be illustrated as in Fig. 1.

An increase in polarizability effect of R' should decrease the ϱ^* and hence the fol-
lowing ordering of polarizability of R' can be established: t-C_4H_9 < i-C_3H_7 ~

Table II
Results of Correlation with Equation (2)

Set	ϱ^*	h^a	r^b	C	R^c
t-BuOR	127·73	12·86	0·953	290·08	t-Bu, i-Pr, n-Pr, Et, Me, H, All, Bz, Cl(CH$_2$)$_2$, HCl$_2$CCH$_2$, Prpg, Cl$_3$CCH$_2$
i-PrOR	104·74	7·91	0·978	277·32	t-Bu, i-Pr, n-Pr, Et, H, All, Bz, Cl(CH$_2$)$_2$, Prpg, ClCH$_2$
c-HexOR	109·09	8·47	0·986	284·34	t-Bu, Me, H, All, Cl(CH$_2$)$_2$, Prpg, ClCH$_2$
EtOR	102·49	6·73	0·983	264·95	t-Bu, i-Pr, n-Bu, n-Pr, Et, H, All, Cl(CH$_2$)$_2$, Prpg, ClCH$_2$
MeOR	110·00	7·87	0·980	256·72	t-Bu, n-Bu, n-Pr, Me, H, All, Bz, Cl(CH$_2$)$_2$, Prpg, ClCH$_2$
PhCH$_2$OR	76·52	9·32	0·951	244·98	t-Bu, i-Pr, n-Pr, Me, H, All, Bz, Cl(CH$_2$)$_2$, Prpg, ClCH$_2$
CH$_2$=CHCH$_2$OR	99·56	5·91	0·985	248·40	t-Bu, i-Pr, Et, Me, H, All, Bz, Cl(CH$_2$)$_2$, Prpg, ClCH$_2$
Cl(CH$_2$)$_2$OR	99·00	6·47	0·982	221·16	t-Bu, i-Pr, n-Pr, Et, Me, H, All, Bz, Cl(CH$_2$)$_2$, Prpg, CF$_3$CH$_2$, ClCH$_2$
HC≡CCH$_2$OR	76·90	7·73	0·962	207·96	t-Bu, i-Pr, n-Bu, n-Pr, Et, Me, H, All, Bz, Cl(CH$_2$)$_2$, Prpg
CH$_2$=CHOR	89·98	5·08	0·993	151·22	t-Bu, i-Pr, n-Bu, n-Pr, Et, Cl(CH$_2$)$_2$, Br(CH$_2$)$_2$, F(CH$_2$)$_2$, I(CH$_2$)$_2$
PhOR	61·47	3·88	0·986	158·23	n-Bu, n-Pr, Et, Me, H, All, Br(CH$_2$)$_2$, Prpg
ClCH$_2$OR	33·15	7·45	0·912	139·01	i-Pr, Et, Me, All, Cl(CH$_2$)$_2$, ClCH$_2$
HOR	91·67	5·30	0·982	220·77	t-Bu, i-Pr, n-Pr, Et, Me, Bz, All, Cl(CH$_2$)$_2$, Br(CH$_2$)$_2$, Cl$_2$CHCH$_2$, Cl$_3$CCH$_2$

[a] Standard error of the ϱ^*. [b] Correlation coefficient. [c] All, Bz and Prpg designate allyl, benzyl, and propargyl respectively; σ^* for HC≡CCH$_2$ was assessed from the basicity data in this work as 0·51, the other σ^*'s were taken from ref.[41].

$\sim$ c-C_6H_{11} $\sim$ C_2H_5 $\sim$ CH_3 $\sim$ $H_2C{=}CHCH_2$ $\sim$ $Cl(CH_2)_2$ < $C_6H_5CH_2$ < C_6H_5 < < $ClCH_2$.

However, the σ^* constants, based on those the polarizability ordering has been established, appear to reflect not only the polar effect, but its blend with polarizability effect. Thus, *e.g.* in a series of similar reactions proceeding under identical conditions, different ϱ constants are claimed to arise from an unequal transmission of electronic effect to a reaction site, i.e. in other words, from different polarizability of the moiety to which a reaction site and a substituent are attached. In the case of substituents bonded directly to a reaction center it has to be their polarizability which differentiates the ϱ's of the above reactions.

Polarizability effect has been originally ascribed to an extra polarization arising during activation of a molecule up to the transition state in consequence of the electronic demand of the reaction center and has been suggested to realize by the inductive or conjugative mode of electron displacement[28]. Since the time variations of the electronic effect of a substituent have been suggested even for the ground state of some molecules, or conjugate acid and base, for its documentation the so-called saturation effect[8,29,30] and very significant dependences of the resonance[31-34] and the polar[31,35] effects upon structural types serve as the best examples. In harmony
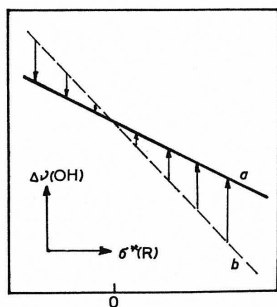
FIG. 1

Schematic Manifestation of the Polarizability Effect of R′ Group in R—O—R′ As Seen from the $\Delta\nu$(OH) *vs* $\sigma^*_{(R)}$ Relationship

a Plot found, polarizability effect of R′ involved, *b* hypothetical plot resulting from the operation of pure polar effect of R′ group.

FIG. 2

The $\varrho^* - \sigma^*$(R′) Dependence

$\varrho^* = 103\cdot53 - 55\cdot77\sigma^*$(R′); correlation coefficient $0\cdot898$.

with that mentioned above, the electronic effect of some substituents, if being visualized as a blend of polar and polariz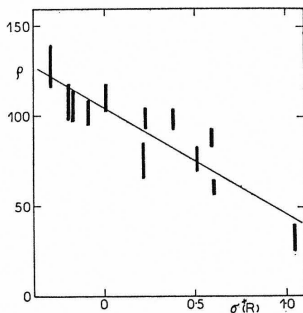ability effects, can be suggested to alter in the transition state, a complex, or even in a molecule in its ground state, or its conjugate acid and base, thanks to the ability of the latter component to answer the electronic demand of an adjacent center.

An "additional" effect appearing during activation process, *i.e.* in the transition state[36,37], or in a complex[21,38], a molecule in its ground state, and conjugate acid or base can be suggested to depend on a substituent itself, position and mode of its attachment to center (probe), and mechanism by which it realizes.

As to the polarizability effect of substituents bonded to oxygen in ethers, general trend of enhanced R' polarizability on going from t-C_4H_9 to more electron-withdrawing substituents is seen from Fig. 2. The linear relationship between ϱ^* (presumably affected only by polarizability effect of R') and σ^* of R' (reflecting the entire electronic effect) implies that polarizability effect of R' is either constant for all R' (which cannot be because of different ϱ^*'s), or it is linearly dependent on the polar effect of R'. The latter implication is, certainly, more justified and urges us to suppose that polarization effect is realized by the H—C(O) hyperconjugation that is facilitated by electron-withdrawing parts of R' as *e.g.* $HC=CH_2$, $HC\equiv C$ and Cl are. Polarizability effect of phenyl group is apparently due to an easy π-electron delocalization. An alternative explanation of great polarizability of $ClCH_2$ group may also consist in an interaction between molecular orbitals localized on the chlorine and the oxygen.

The polarizability order of R' groups in ROR' established in this work using the data for equilibrium (A) looks not as it could be expected on the basis of the measurements of equilibrium data[39,40] on alkanols and ethers with other reference acids. Despite that proper polarizability effect of groups is not known, polarizability of alkyl groups bonded to oxygen is suggested to be enhanced by their size and branching[39,40]. There are no other reports on polarizability effect of other groups bonded to oxygen, but extensive study of molecular effects on the gas-phase equilibrium data of amines enabled Taft and his associates[8] to state that „stabilization by polarization of saturated and unsaturated molecular cavities B of the conjugate (BH^+) appears to be essentially the same for equal carbon content and similar framework" and that the degree of downchain hydrogenation of molecular cavity is of minor, if any, importance in determining its polarizability effect. (Different polarizability effect of the phenyl and cyclohexyl groups found in this work sounds therefore surprisingly.) In order to find a plausible explanation for the ordering of group polarizability in ethers established in this work, we have to postulate that the mechanism of polarization effect depends on the electronic demand of a center to be stabilized. It would mean that the C—H hyperconjugation mechanism of the polarizability effect stabilizing electron-deficient oxygen dominates in complex ROR'...C_6H_5OH and other mechanism (presumably induced dipole-charge interaction) is operative to stabilize an oxygen with greater electron deficiency in conjugate acid of ether.

The above postulate and the following consideration are lacking experimental evidence, but are consonant with the interpretation of the observations[21,40] that basicity of some ethers is dependent on the type and strength of the reference acid. To quote Pitt and coworkers[21]:" conjugative delocalization of the lone pair electron density in siloxanes and anisol is largely responsible for the low basicity toward weak acids, but becomes less important as the stronger acid polarises the total electron distribution of the base".

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Translated by the author (J. P.).