group R and the change in six-number (Δx) of the group between an acyl and a nonacyl environment (eq 7). The

$$\log k = 1.02E_s' + 0.916(\Delta x) + 0.867 \qquad r = 0.994 \qquad \psi = 0.135 \tag{7}$$

hydrolysis of symmetrically substituted alkyl carboxylates[3] (RCO_2R) is likewise amenable to such a treatment. For symmetry reasons only two parameters are necessary: an E_s' term which represents the combined steric effects of R in its acyl and nonacyl environment and Δx. This yields eq 8. Thus it appears that the steric effects of alkyl groups

$$\log k = 2.44E_s' + 1.29\Delta x + 0.804 \qquad r = 0.994 \qquad \psi = 0.136 \tag{8}$$

in the nonacyl portion of an ester are adequately taken into account by E_s' and Δx steric parameters.

Overview

The revised Taft steric parameter[5a] E_s' is based on the Taft–Ingold hypothesis and is calculable directly from the rate constants for acid-catalyzed esterification of carboxylic acids in methanol at 40 °C. Hancock-type parameters are *derived* from these by means of the correction term $0.306(n_H - 3)$. It is shown that the use of such derived parameters does not improve the different correlations where steric effects either are taken care of by straightforward Taft-type parameters or are used in a manner where conformational orientations and terminal site effects (Δx) are carefully considered.

Though this analysis shows no need for the Hancock data treatment, it does not exclude the existence of hyperconjugation effects in certain cases. Their role, however, becomes more difficult to identify and estimate in the esterification reactions, particularly so if one points to the behavior of the methyl group in our totally steric interpretation. One would expect this E_s' value to drop out of the general correlation. In fact, such is not the case, and this observation may be considered as a strong argument against the need for correction, implying a hyperconjugative interpretation.

The different models considered favor the hypothesis of a complex behavior of pure steric parameters. This is further backed by the coherence of these conclusions with Charton's point of view.[11] There is, in fact, an excellent correlation between E_s' and the van der Waals radius, $r_{v,\min}$, of Charton for symmetrical groups: for the groups H, Me, *t*-Bu, Cl_3C, and Br_3C the correlation is excellent, $r = 0.99993$ and $\psi = 0.015$, for an E_s' variation of greater than three units. For these simple symmetrical groups, where the subgroups are indistinguishable and proximity site effects (six-number) are absent, the interpretation of E_s' in terms of $r_{v,\min}$ confirms the very general treatment based on pure steric factors (eq 7 and 3).

It is noteworthy that for all simple groups, symmetrical and nonsymmetrical, a physical interpretation of E_s' in terms of site, bond, and angle interaction functions can be developed by means of a molecular mechanics (MM) treatment,[12] whereas all our data handling has been inspired by the chemist's usual data compression, i.e., visualization of subgroups, conformations, and specific site effects. Both treatments have complementary merits for usual environments, but for complex ones with extremely large E_s' values where no valid MM parameters are available, the steric hindrance "subgroup additivity plus topology model" seems to yield more than reasonable success for interpretation and prediction purposes.

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Structural Effects on the Reactivity of Ethers in Donor-Acceptor Reactions

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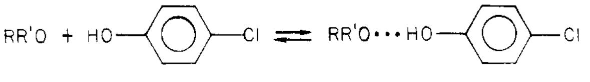
As indicated by West and co-workers[2] and by Arnett,[3] it seems fairly well established that donor–acceptor interactions (either through hydrogen bonding or charge transfer) of ethers are quite sensitive to both steric and electronic effects. In order to help unravel the contributions from these effects we present here new data for two simple reactions: (1) the hydrogen-bonding complexing of several cyclic and acyclic ethers with *p*-chlorophenol in dilute solution in cyclohexane (the equilibrium constants, *K*, for process 1 have been measured at 20 °C by UV absorption spectrometry; the experimental results are given in Table I); (2) the gas-phase protonation of some selected ethers. Their basicities relative to ammonia, i.e., the free energies of reaction 2, have been determined by ion cyclotron resonance spectroscopy (ICR).[4] These free energies, ΔG°, and the corresponding equilibrium constants, K_p, are summarized in Table II.



(1)

$$NH_4^+ + RR'O \rightleftarrows RR'OH^+ + NH_3 \tag{2}$$

Discussion

Rather than attempting to undertake a full quantitative structure–reactivity study, we shall focus attention on some conspicuous features of these sets of results.

(1) The values of *K* for cyclic ethers are systematically higher than those for the acyclic compounds of same carbon content. More precisely, for compounds having the same carbon content and the same degree of branching, the ratio $K_{\text{cyclic}}/K_{\text{acyclic}}$ takes values of 2–3 (Table III).

(2) Consider now a series of acyclic ethers, ROR′, in which the substituent R is kept constant while the R′ moiety undergoes successive α-methyl substitutions. On a quantitative basis, the effects of these substitutions on the constant *K* are quite small, frequently of the order of magnitude of experimental error. Typical results follow: $K_{\text{EtO-}n\text{-Pr}}/K_{\text{MeO-}n\text{-Pr}} = 1.11 \pm 0.07$, $K_{i\text{-PrO-}n\text{-Pr}}/K_{\text{EtO-}n\text{-Pr}} = 0.95 \pm 0.06$, $K_{t\text{-BuO-}n\text{-Pr}}/K_{i\text{-PrO-}n\text{-Pr}} = 0.92 \pm 0.06$. On the other hand, $(t\text{-Bu})_2O$, relative to other members of the RO-*t*-Bu family, is an important exception: while $K_{\text{EtO-}t\text{-Bu}}/K_{\text{MeO-}t\text{-Bu}} = 1.03 \pm 0.06$ and $K_{i\text{-PrO-}t\text{-Bu}}/K_{\text{EtO-}t\text{-Bu}} = 1.04 \pm 0.06$, one finds $K_{(t\text{-Bu})_2O}/K_{i\text{-PrO-}t\text{-Bu}} = 0.39 \pm 0.03$. In the cyclic series, the effect is a sizable, but seemingly not additive, increase

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Table I. Equilibrium Constants for Reaction 1, Hydrogen-Bond Formation between Various Ethers and *p*-Chlorophenol, in Cyclohexane at 20 °C in the Mole Fraction Scale

ether	$10^{-2}K$
MeO-*n*-Pr	1.87 ± 0.06
MeO-*n*-Bu	1.87 ± 0.06
MeO-*i*-Bu	1.80 ± 0.06
MeO-*s*-Bu	2.31 ± 0.07
MeO-*t*-Bu	2.63 ± 0.07
EtOEt	2.49 ± 0.08
EtO-*n*-Pr	2.08 ± 0.06
EtO-*i*-Pr	2.49 ± 0.08
EtO-*n*-Bu	1.80 ± 0.06
EtO-*s*-Bu	2.27 ± 0.07
EtO-*t*-Bu	2.71 ± 0.09
n-PrO-*n*-Pr	1.64 ± 0.05
n-PrO-*i*-Pr	1.98 ± 0.06
n-PrO-*t*-Bu	1.82 ± 0.06
i-PrO-*i*-Pr	2.84 ± 0.09
i-PrO-*n*-Bu	1.98 ± 0.06
i-PrO-*t*-Bu	2.82 ± 0.09
n-BuO-*n*-Bu	1.61 ± 0.05
t-BuO-*t*-Bu	1.10 ± 0.03
oxetane	5.8 ± 0.2
THF	5.1 ± 0.2
2-MeTHF	6.2 ± 0.2
2,2-Me_2THF	6.6 ± 0.2
tetrahydropyran	4.4 ± 0.1
oxepane	5.0 ± 0.2

Table II. Gas-Phase Basicities Relative to Ammonia of Selected Ethers at 300 K

ether	$\Delta G°$, kcal/mol[a]	*K*p[b]	ref
MeOMe	11.0 ± 0.2	$(9.8 \pm 3.4) \times 10^{-9}$	4
MeOEt	7.5 ± 0.2	$(3.5 \pm 1.4) \times 10^{-6}$	4
OXT			5
EtOEt	3.7 ± 0.2	$(2.0 \pm 0.8) \times 10^{-3}$	4
THF	4.7 ± 0.2	$(3.8 \pm 1.5) \times 10^{-4}$	4
EtO-*i*-Pr	0.8 ± 0.2	$(2.6 \pm 1.0) \times 10^{-1}$	4
2-MeTHF	1.2 ± 0.2	$(1.3 \pm 0.5) \times 10^{-1}$	6
EtO-*t*-Bu	−1.8 ± 0.2	20 ± 8	6
2,2-Me_2THF	−0.9 ± 0.2	4.5 ± 1.8	6
THP	4.0 ± 0.2	$(1.2 \pm 0.5) \times 10^{-3}$	4
n-PrO-*n*-Pr	1.8 ± 0.2	$(3.2 \pm 1.3) \times 10^{-2}$	7
OXP	2.5 ± 0.2	$(1.5 \pm 0.6) \times 10^{-2}$	7

[a] Standard free energy of reaction 2, kcal mol^{-1}. [b] Equilibrium constant for reaction 2.

Table III. Values of $K_{cyclic}/K_{acyclic}$ for the Reaction of Various Cyclic and Acyclic Ethers Having the Same Carbon Content and Degree of Branching with *p*-Chlorophenol in Cyclohexane at 20 °C

ethers couple (cyclic/acyclic)	$K_{cyclic}/K_{acyclic}$
OXT/MeOEt	2.3[a]
THF/EtOEt	2.1 ± 0.1
THP/EtO-*n*-Pr	2.1 ± 0.1
2-MeTHF/EtO-*i*-Pr	2.5 ± 0.1
2,2-Me_2THF/EtO-*t*-Bu	2.5 ± 0.1
OXP/*n*-PrO-*n*-Pr	3.0 ± 0.2

[a] Since MeOEt is a gas at 20 °C, the value of *K* for this compound has been estimated from the data given in ref 12.

Table IV. Enthalpies of Association, $\Delta H°$, between Selected Ethers and Phenols

ether	phenol	solvent	$\Delta H°$, kcal/mol	ref
EtOEt	PCP[a]	c-C_6H_{12}	−7.3 ± 0.4[c]	13
THF	PCP	c-C_6H_{12}	−7.3 ± 0.4[c]	13
EtO-*n*-Pr	PCP	c-C_6H_{12}	−6.5 ± 0.4[c]	13
THP	PCP	c-C_6H_{12}	−6.9 ± 0.4[c]	13
MeO-*t*-Bu	PCP	c-C_6H_{12}	−8.2 ± 0.4[c]	13
EtO-*t*-Bu	PCP	c-C_6H_{12}	−8.4 ± 0.4[c]	13
EtOEt	PFP[b]	CCl_4	−5.57 ± 0.05[d]	14
THF	PFP	CCl_4	−5.75 ± 0.05[d]	14
EtOEt	phenol	CCl_4	−5.45 ± 0.05[d]	14
THF	phenol	CCl_4	−5.57 ± 0.05[d]	14

[a] *p*-Chlorophenol. [b] *p*-Fluorophenol. [c] Spectrometric determination. [d] Calorimetric determination.

Table V. Infrared Frequency Shifts, $\Delta\nu_{OH}$, of the OH Stretching Band of Phenol Hydrogen Bonded to Various Ethers in Carbon Tetrachloride Solution[a]

ether	$\Delta\nu_{OH}$, cm^{-1}
OXT	282[b]
EtOEt	280 ± 3
THF	287 ± 3
EtO-*n*-Pr	272[b]
THP	290[b]
n-BuO-*n*-Bu	285 ± 2
EtO-*t*-Bu	298 ± 1
t-BuO-*t*-Bu	321 ± 4

[a] Data from Koppel and Paju.[15] [b] Error limits not given in the original reference.

of the constant: $K_{2\text{-MeTHF}}/K_{THF} = 1.21 \pm 0.07$ and $K_{2,2\text{-Me}_2\text{THF}}/K_{THF} = 1.31 \pm 0.08$.

(3) The ratios $K_{RO\text{-}n\text{-}Pr}/K_{ROEt}$ and $K_{RO\text{-}n\text{-}Bu}/K_{ROEt}$ are consistently smaller than 1; for example: $K_{EtO\text{-}n\text{-}Pr}/K_{Et_2O} = 0.84 \pm 0.05$ and $K_{EtO\text{-}n\text{-}Bu}/K_{Et_2O} = 0.72 \pm 0.04$. The largest effect corresponds to the compounds in which R = *t*-Bu: $K_{n\text{-}PrO\text{-}t\text{-}Bu}/K_{EtO\text{-}t\text{-}Bu} = 0.67 \pm 0.03$.

(4) It is particularly significant that, among the 25 association constants given in Table I, the largest one corresponds to oxetane (OXT), the smallest, least crowded molecule, while the smallest one corresponds to the highly crowded, heavily substituted $(t\text{-Bu})_2O$. The above results clearly hint at some steric influences.[8] It should not be overlooked, however, that cyclic ethers have dipole moments which are higher than those of the acyclic compounds of the same carbon content.[9] They also have higher "bulk polarities" (as measured, for example, by the π^*[10] or E_T[11] parameters). It therefore seems necessary to eliminate dipolar interactions as the source of these effects.

First and foremost, the enthalpies of association by hydrogen bonding between different proton donors and cyclic ethers in inert solvents are extremely close in absolute value to those corresponding to the same proton donors with acyclic ethers of the same carbon content. Some representative values are shown in Table IV.

Further evidence is provided by NMR studies. Thus, significant values of the limiting chemical shifts (δ) of the proton of chloroform hydrogen bonded to ethers in cyclohexane solution relative to "free" chloroform[13] are: THF (0.86 ± 0.02), Et_2O (0.83 ± 0.07), THP (0.80 ± 0.05),

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[8] They are reminiscent of the results obtained by Covitz and Westheimer [F. Covitz and F. H. Westheimer, *J. Am. Chem. Soc.*, **85**, 1773 (1963)] in their studies of steric effects in general basic catalysis. Thus, it has been shown by these authors that 2,6-lutidine is a much weaker catalyst than 2,4-lutidine, although they are of comparable base strength and, similarly, 2,4-lutidine is a poorer catalyst relative to 3-picoline than can be anticipated from their base strengths. We are indebted to a referee for pointing out these analogies.

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Table VI. Effects of the Steric Requirements of the Electron Acceptor on the Relative Reactivity of Ethers

electron acceptor	$K_{THF}/K_{(i\text{-}Pr)_2O}$	$K_{THP}/K_{(i\text{-}Pr_2)O}$	solvent (temp, °C)	ref
PCP[a]	1.8 ± 0.1	1.5 ± 0.1	c-C_6H_{12} (20)	6
Cl_3CH	1.5 ± 0.3	1.3 ± 0.3	c-C_6H_{12} (34.5)	13
I_2	3.3 ± 0.6	3.5 ± 0.6	c-C_6H_{12} (20)	17
BF_3	16×10^{3}[b]	2.4×10^{3}[b]	C_6H_6 (27)	18

[a] *p*-Chlorophenol. [b] Uncertainty estimated at ca. 20%.

EtO-*n*-Pr (0.87 ± 0.08), *i*-Pr_2O (0.91 ± 0.07), EtO-*t*-Bu (0.99 ± 0.07). Here, again, the values of δ for acyclic straight-chain ethers and for their cyclic homologues are very close.

The infrared frequency shifts ($\Delta\nu_{OH}$) of the OH stretching band of hydrogen-bonded phenol in carbon tetrachloride solutions display a similar pattern, as indicated in Table V which contains recent data from Koppel and Paju.[15] Although here the shifts are somewhat higher for the cyclic ethers than for the acyclic compounds of the same carbon content, probably as a consequence of the higher polarity of the cyclic compounds, two results still remain valid. (a) The quantitative ranking of the shifts for cyclic ethers is OXT (oxetane) < THF (tetrahydrofuran) < THP (tetrahydropyran), exactly the opposite to that obtained on the basis of K. (b) The order of magnitude of these effects for cyclic ethers is comparable to that of the straight-chain acyclic homologues and smaller than those induced by ethers with branched side chains. Both the results from IR and NMR studies are perfectly consistent with a conclusion drawn by Gurka and Taft,[16] namely that formation constants for donor–acceptor equilibria are more sensitive to steric factors than the NMR (or IR) shifts.

It can also be expected that the selectivity in favor of the cyclic ethers will increase with the severity of the steric requirements imposed by the size and shape of the electron acceptor. Although data are somewhat scarce, we have attempted to illustrate this effect by comparing the ratios of the equilibrium constants for the couples, THF/(*i*-Pr)$_2$O and THP/(*i*-Pr)$_2$O, associated with four different electron acceptors. The results are given in Table VI.

Finally it can be ruled out that cyclic ethers are better able to stabilize positive charges on the oxygen than are the corresponding acyclic compounds. Such a possibility is conclusively shown not to be involved by comparing the gas-phase basicities of some selected ethers. These results have been recently obtained[4,6,7] by means of ion cyclotron resonance spectroscopy. Inasmuch as the gas-phase basicities of ethers and amines appear to be remarkably free of steric influences,[19] they are a trustworthy measure of the ability of the substituents R and R′ to stabilize a formal positive charge borne by the oxygen atom in the ions $RR'OH^+$ generated in the gas phase. The free energies of reaction 2 are given in Table II. From these results the following conclusions can be drawn. (a) Without any known exception, the basicity of a cyclic ether is smaller than that of the corresponding acyclic compound of the same branching and carbon content. (b) α-, β-, or γ-methyl substitution invariably increases the basicity of both cyclic and acyclic ethers. (c) The basicity of cyclic ethers regularly increases with the ring size: THF < THP < OXP (oxepane) (while, according to K, the effect of ring size is OXT > THF > OXP > THP).

As a conclusion, the steric effect appears to be a decisive factor determining (a) the enhanced reactivity of cyclic ethers relative to their acyclic homologues in reactions involving uncharged donor–acceptor processes in solution and (b) the influence of the ring size on the reactivity of cyclic ethers. A detailed quantitative dissection of the contributions of steric and electronic effects to the donor–acceptor properties of acyclic ethers, involving a wider range of substituents, will be carried out in a future paper.

Experimental Section

Materials. The origin and purification of ethers, according to standard procedures, have been described elsewhere.[4,12] The cyclohexane used in the spectrometric measurements was Merck "Uvasol", refluxed over and distilled from a liquid sodium–potassium alloy. *p*-Chlorophenol, of the highest commercial purity, was vacuum distilled and twice crystallized from dry cyclohexane.

ICR Measurements. These have been carried out at 300 K with the U. C. Irvine pulsed ion cyclotron resonance spectrometer.[20] A detailed discussion of the procedure used is found in ref 4, 8, and 20. Typical uncertainties on the free energies are ± 0.2 kcal mol^{-1}.

UV Measurements. These experiments have employed a Beckman DK2 and a Beckman Acta V spectrophotometer with matched 5-cm silica window cells. The temperature was kept constant by means of water circulation through the cell holder. The mole fractions of *p*-chlorophenol and ethers were kept below 5×10^{-5} and 5×10^{-2}, respectively. The equilibrium constants were measured by a technique used in a number of previous studies.[12,17,21] The constants were first determined by a graphical method[22] derived from that of Nagakura[23] and were further optimized by least squares. The results are estimated to be precise within 3%.

Acknowledgment. We wish to acknowledge the valuable assistance of Dr. C. Kraus-Benamou.

Registry No. MeO-*n*-Pr, 557-17-5; MeO-*n*-Bu, 628-28-4; MeO-*i*-Bu, 625-44-5; MeO-*sec*-Bu, 6795-87-5; MeO-*t*-Bu, 1634-04-4; EtOEt, 60-29-7; EtO-*n*-Pr, 628-32-0; EtO-*i*-Pr, 625-54-7; EtO-*n*-Bu, 628-81-9; EtO-*sec*-Bu, 2679-87-0; EtO-*t*-Bu, 637-92-3; *n*-PrO-*n*-Pr, 111-43-3; *n*-PrO-*i*-Pr, 627-08-7; *n*-PrO-*t*-Bu, 29072-93-3; *i*-PrO-*i*-Pr, 108-20-3; *i*-PrO-*n*-Bu, 1860-27-1; *i*-PrO-*t*-Bu, 17348-59-3; *n*-BuO-*n*-Bu, 142-96-1; *t*-BuO-*t*-Bu, 6163-66-2; oxetane, 503-30-0; THF, 109-99-9; 2-MeTHF, 96-47-9; 2,2-Me$_2$THF, 1003-17-4; tetrahydropyran, 142-68-7; oxepane, 592-90-5; MeOMe, 115-10-6; MeOEt, 540-67-0; *p*-chlorophenol, 106-48-9; *p*-fluorophenol, 371-41-5; phenol, 108-95-2.

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