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Heats of Hydrogenation of Some Vinyl Ethers and Related Compounds

N. L. Allinger,* John A. Glaser, and H. E. Davis

Department of Chemistry, University of Georgia, Athens, Georgia 30602

Donald W. Rogers†

Department of Chemistry, Brooklyn Center, Long Island University, Brooklyn, New York 11201

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The heats of hydrogenation of a number of vinyl ethers and related compounds have been measured in hexane solution. The presence of the oxygen has a small to moderate effect on the magnitudes of these numbers, depending on the situation, and may either stabilize or destabilize the double bonds relative to the hydrogenation products. The results can, in the main, be interpreted in a straightforward way using resonance and induction arguments.

A favorite technique for thermochemical studies involving unsaturated hydrocarbons is measurement of their heats of hydrogenation.[1] Many high-quality gas-phase measurements were reported by Kistiakowsky in the 1930's,[2] and subsequently a large volume of work was published by Turner and his collaborators,[3] mainly in the 1950's and 1960's. While the measurements by Turner seem to be quite reliable, he used acetic acid as the hydrogenation solvent. Alkenes, being bases, tend to have somewhat less endothermic heats of solution in acetic acid (from hydrogen bonding) than do the alkanes to which they hydrogenate. This results in systematically less exothermic heats of hydrogenation in acetic acid than the desired gas-phase values by an amount approximately equal to the endothermic heat of dissociation of the solvent–alkene complex.[4b]

In contrast to the unsaturated hydrocarbons, reported heats of hydrogenation of molecules other than hydrocarbons have been relatively few.[1] The present paper describes measurement of these heats for a number of oxygen-containing molecules, which also contain a carbon–carbon double bond that can be reduced. In each case, the reaction was carried out in a very dilute hexane solution, so that solvation problems were minimized. We believe that the process of hydrogenating molecules in dilute solution, widely separated by inert solvent molecules, is not physically very different from hydrogenating them in the gas phase and we have recently published evidence to support this view.[4b]

The calorimeter and the experimental procedure have been subjected to modifications over the years. For current descriptions, see ref 4. Experimental values are given in Table I for the heats of hydrogenation measured in the present work.

The enthalpies of hydrogenation (gas phase, 82 °C) of ethylene, 1-butene, and *trans*-2-butene to the corresponding alkanes are[5] −32.8, −30.3, and −27.6 kcal/mol, respectively. These examples demonstrate that, in the absence of special steric or resonance interactions, the stabilizing effect of an alkyl group relative to hydrogen on a carbon–carbon double bond is about 2.5 kcal/mol. The ethoxy group of ethyl vinyl ether (1) lowers the enthalpy of hydrogenation[6] to −26.7 kcal/mol (also in the gas phase, 82 °C). The values given in Table I for this compound have a mean of −26.5 kcal/mol and a probable error of ±0.3 kcal/mol. Kistiakowsky's value of −26.7 kcal/mol is not strictly comparable because of the different temperatures, 82 and 25 °C. An approximate correction can be made by appplying Kirchoff's equation[7] and taking −4 cal/(mol K) as the ΔC_p of the reaction, which leads to a correction of +0.2 kcal/mol for the earlier number, changing it also to −26.5 kcal/mol.

Table I. Heats of Hydrogenation (kcal/mol)

no.	compd	$-\Delta H$
1	ethyl vinyl ether[a]	26.23 (0.10)[b] 26.77 (0.18)
2	1,4-bis(vinyloxy)butane[c]	52.76 (0.36) 53.33 (0.27)
3	bis[(vinyloxy)ethyl] ether[c]	54.28 (0.50) 53.13 (0.36)
4	dihydropyran	24.87 (0.28) 24.52 (0.21)
5	3,4-dihydro-2-methoxy-2*H*-pyran	25.71 (0.26) 26.07 (0.30)
6	5,6-dihydro-4-methoxy-2*H*-pyran[c]	23.31 (0.24) 22.91 (0.15)
7	9-oxabicyclo[3.3.1]non-1-ene[c]	37.13 (0.21) 36.82 (0.20)
8	3-oxacyclopentene	25.83 (0.36) 25.30 (0.24)
9	4-oxacyclopentene	27.67 (0.30) 28.28 (0.33)
10	2,5-dimethoxy-2,5-dihydrofuran	31.65 (0.19) 31.10 (0.10)

[a] A literature value for this compound is available, 26.7 kcal/mol[6] (gas phase, 82 °C). [b] Numbers in parentheses are 95% confidence limits for individual runs. Probable errors are estimated to be twice these values. [c] The compound showed slight turbidity during sample preparation (see Discussion).

The temperature correction factor, +0.2 kcal/mol, applies to most simple molecules, specifically ethylene, 1-butene, and *trans*-2-butene mentioned above. This correction is probably not necessary in cases like the present one for which the experimental uncertainty is larger than the correction but it illustrates two points that should be made: (1) it is small and (2) it is substantially the same for most hydrogenations. This means that qualitative

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† Currently on leave at Barnard College, New York, NY 10027

(1) For a review, see J. L. Jensen, *Prog. Phys. Org. Chem.*, 12, 189 (1976).

(2) J. B. Conn, G. B. Kistiakowsky, and E. A. Smith, *Discuss. Faraday Soc.*, 61, 1868 (1939), and earlier papers.

(3) R. B. Turner, B. J. Mallon, M. Tichy, W. von E. Doering, W. R. Roth and C. Schröder, *J. Am. Chem. Soc.*, 95, 8605 (1973), and earlier papers in this series.

(4) (a) D. W. Rogers, P. M. Papadimetriou, and N. A. Siddiqui, *Mikrochim. Acta*, 389 (1975); (b) D. W. Rogers, O. A. Dagdagan, and N. L. Allinger, *J. Am. Chem. Soc.*, 101, 671 (1979).

(5) J. B. Conant and G. B. Kistiakowsky, *Chem. Rev.*, 20, 181 (1937).

(6) M. A. Dolliver, T. L. Gresham, G. B. Kistiakowsky, and W. E. Vaughan, *J. Am. Chem. Soc.*, 59, 831 (1937).

(7) J. D. Cox and G. Pilcher, "Thermochemistry of Organic and Organometallic Compounds", Academic Press, London, 1970, p 14.

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generalizations like the ones in the preceeding paragraph drawn from experiments at 82 °C hold equally well at 25 °C. We may thus state that the ethoxy group stabilizes the double bond by about 6.1 kcal/mol, relative to hydrogen, or 3.6 kcal/mol more than does a methyl group. The greater stabilization of the double bond by the ethoxy group can be rationalized in terms of the resonance between the double bond and the lone pair of π electrons on oxygen.

$$CH_3CH_2{-}O{-}CH{=}CH_2 \leftrightarrow CH_3CH_2{-}\overset{+}{O}{=}CH{-}CH_2^-$$

The next two compounds listed in Table I, 1,4-bis(vinyloxy)butane (2) and bis(vinyloxy)ethyl ether (3), have heats of hydrogenation of −53.0 and −53.7 kcal/mol, respectively. These quantities are substantially twice that for ethyl vinyl ether itself, indicating that no special resonance or other effects are present in these compounds, insofar as one can see from the heats of hydrogenation.

Kistiakowsky has obtained a value of −57.2 kcal/mol^{-1} for the hydrogenation of divinyl ether, 4.2 kcal/mol^{-1} more exothermic than that for 2 and 3.5 kcal/mol^{-1} more exothermic than that for 3. In divinyl ether the oxygen atom's electrons are shared in conjugative interaction with both vinylic groups, decreasing their effectiveness in stabilizing either one. The heat of hydrogenation of divinyl ether lies between those of the bis(vinyloxy) compounds and that of an alkadiene containing two terminal double bonds separated by a C_2H_4 or longer chain, e.g., hexa-1,5-diene, in which the double bonds are essentially independent of one another and no oxygen is present.

$CH_2{=}CHOCH_2CH_3$

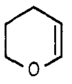
1

$CH_2{=}CHOCH_2CH_2CH_2CH_2OCH{=}CH_2$

2

$CH_2{=}CHOCH_2CH_2OCH_2CH_2OCH{=}CH_2$

3



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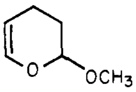

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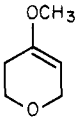

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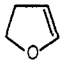

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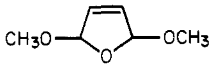
9

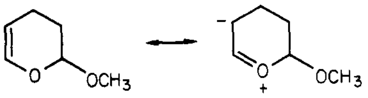


10

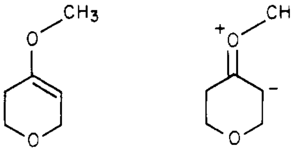
Dihydropyran (4) is the first example we come to in Table I where the vinyl ether is confined to a ring, thus diminishing the possibility of conformational isomerism. Lord, Rounds, and Ueda[8] reported the molecule exists in a twisted (half-chair) conformation. Within the context of the usual sp^2–p hybrid picture of bonding in alkenes, this would necessarily lead to a partial disruption of the conjugation of the p electrons on oxygen with the double bond. The measured enthalpy of hydrogenation (−24.7 kcal/mol) is somewhat smaller in magnitude than that for ethyl vinyl ether. However, we might anticipate that substitution of the alkyl group onto the double bond in a position providing no hindrance (which we will assume is a condition satisfied by the ring) should lower the magnitude of the heat of hydrogenation from 26.5 to 24.0 kcal/mol. The experimental value is a little larger, which would be consistent with a small disruption of the π system, and a concomitant loss in resonance energy. An alternative view would be the following. The heat of hydrogenation of cyclohexene is −28.6 kcal/mol at 82 °C, which is the same as that of *cis*-2-butene and 1.0 kcal/mol larger in magnitude than that of the trans isomer. We might thus expect in dihydropyran a heat of hydrogenation which is 1.0 kcal/mol greater in magnitude than that arrived at above, namely, −25.0 kcal/mol. In this case the calculated value is larger in magnitude than the experimental value by 0.3 kcal/mol, which is within experimental error. According to this view, dihydropyran is quite normal and shows no measurable steric or resonance effect that differs significantly from what would be expected by elementary considerations.

Next we come to 3,4-dihydro-2-methoxy-2*H*-pyran (5), for which the measured heat of hydrogenation is −25.9 kcal/mol. This compound has a heat of hydrogenation which is more exothermic than that of the corresponding dihydropyran by 1.2 kcal/mol.

Elementary considerations suggest the following. The resonance between the lone pair of electrons on the ring oxygen and the double bond tends to put a positive charge on oxygen relative to the oxygen in tetrahydropyran as shown. The inductive effect of the methoxyl group would withdraw electrons from the carbon to which the two oxygens are attached. This positive charge would tend to suppress the resonance effect of the ring oxygen, thus destabilizing the unsaturated compound. So elementary considerations suggest an effect in the observed direction. The magnitude of the effect is again small, but it seems to be beyond experimental error.



The next entry in Table I, 5,6-dihydro-4-methoxy-2*H* pyran (6), has a heat of hydrogenation which is only −23.1 kcal/mol. In this case the ring oxygen is positioned so as to withdraw electrons by induction from one end of the double bond, which is the end to which they are pushed to by resonance from the methoxyl. The observed effect is in the direction expected from resonance considerations, i.e., here the ring oxygen *stabilizes* the unsaturated compound. Again, the effect is small, but the contrast between the heats of hydrogenation of 5 and 6 is noteworthy.



In keeping with the strain attributed to twisted double bonds at bridgeheads in small bicyclic systems, the heat of hydrogenation of 9-oxabicyclo[3.3.1]non-1-ene is quite large (−36.9 kcal/mol). Chiang, Kresge, and Wiseman[9] estimated a value of 12 kcal/mol for the strain in the corresponding double bond in the parent hydrocarbon, bicyclo[3.3.1]non-1-ene. The somewhat smaller strain here (10.5 kcal/mol) is perhaps due in part to resonance between the oxygen and the double bond, but it is not certain that the difference is really beyond combined experimental errors.

The remaining entries in Table I are 3-oxacyclopentene (8), 4-oxacyclopentene (9), and the 2,5-dimethoxy deriva-

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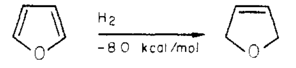
[8] R. C. Lord, T. C. Rounds, and T. Ueda, *J. Chem. Phys.*, 57, 2573 (1972).

[9] Y. Chiang, A. J. Kresge, and J. R. Wiseman, *J. Am. Chem. Soc.*, 98, 1564 (1976).

tive of the latter (**10**). The measured heats of hydrogenation are −25.6, −28.0, and −31.4 kcal/mol, respectively. Cyclopentenes in general have relatively small heats of hydrogenation, because the cyclopentane to which they hydrogenate suffers from rather severe torsional strain.[1] Cyclopentene itself, for example, has a heat of hydrogenation of −26.9 kcal/mol,[1] compared to a less strained cis alkene, cyclohexene, −28.6 kcal/mol. So either **9** has quite a bit of strain induced in it from some source, apart from what is found with cyclopentene, or tetrahydrofuran is relatively more stable than cyclopentane (or both). A stabilizing effect of the oxygen in the 3-position is evident in **8**. It's not obvious what the substitution of a methylene group by an oxygen atom will do to the strain energy in terms of angular and torsional components, and we hope to explore the application of molecular mechanics to this problem later. We may, however, note that the oxygen in **9** should tend to remove electron density from the double bond by induction. Since methyl groups stabilize double bonds by electron donation, it is not surprising that electron withdrawal leads to *destabilization*. For **10** the effect is in the same direction, but stronger, since here there are three oxygens withdrawing electrons.

Conant and Kistiakowsky[5] estimated the degree of participation by oxygen in small-ring conjugation by determining the heat of hydrogenation of furan (−36.63 kcal/mol) and making the approximation that the heat of hydrogenation of 4-oxacyclopentene (2,5-dihydrofuran) would be roughly the same as that for *cis*-2-butene (−28.57 kcal/mol). This leads to −8.0 kcal/mol for the partial hydrogenation of one of the double bonds in furan with migration of the other. A low value for partial hydrogenations of this kind indicates considerable stabilization of the reactant molecule relative to one containing an isolated cis double bond. Indeed, in the classical case of hydrogenating one double bond in benzene to produce cyclohexadiene, the magnitude of the heat of partial hydrogenation is so severely reduced that it changes sign, yielding a predicted endothermic reaction. The present results indicate a moderately stabilizing influence of the oxygen in furan.



A similar estimation procedure for the partial hydrogenation of furan to 3-oxapentene (2,3-dihydrofuran) (**8**) was made by Conant and Kistiakowsky, giving −11.5 kcal/mol.[5] In this case, 2-ethoxypropene was used as the analogue of 2,3-dihydrofuran for estimating the heat of hydrogenation of the latter compound to tetrahydrofuran. The estimated value, −25.1 kcal/mol, was subtracted from the heat of hydrogenation of furan to give the value for partial hydrogenation just cited. Although these guesses were made in the most tentative way more than 40 years ago, our experimental vaues in Table I show both guesses to have been good ones. Conclusions drawn from our experimental data are qualitatively the same as those drawn by Conant and Kistiakowsky; 2,3-dihydrofuran is stabilized relative to 2,5-dihydrofuran, presumably by oxygen acting in a conjugative sense in **8** and in an inductive way in **9**.

Quantitative agreement is good. The original estimated values for the partial hydrogenation of furan to give the 2,5- and 2,3-dihydrofurans were −8.0 and −11.5 kcal/mol, respectively, while the values proceeding from Kistiakowsky's experimental determination for furan and our results for the two dihydrofurans are −8.6 and −11.0 kcal/mol, respectively, without temperature correction of the furan datum. Temperature correction would make agreement better by 0.2–0.4 kcal/mol in the first case and worse by the same amount in the second case.

In hydrogenation of cycloalkenes, the five-membered ring is less exothermic in its reaction than the six-membered ring. This is widely accepted as being due to torsional differences in the product molecules, which outweigh the differences in bending energies, which work in the opposite direction. In five- and six-membered rings containing oxygen, however, the order of exothermicity is reversed. The most likely explanation is that in this case the difference in the bending energies is greater here than in the hydrocarbons due to the fact that bond angles containing oxygen have larger bending force constants (in the MM2 program)[10] than those containing only carbon; so here bending effects outweigh, slightly, torsional effects.

Conclusions. The presence of an ether oxygen in an unsaturated molecule does not prevent one from measuring its heat of hydrogenation under the conditions that we commonly use (room temperature, hexane solvent). The oxygen has a modest effect on the numerical value of the measured heat in many cases, which can be interpreted on the basis of conventional resonance and inductive effects.

Experimental Section

Apparatus. The apparatus and subsequent minor modifications have been described.[4]

Reagents. 1-Hexene, 99.9%, was obtained from Chemical Samples Co. and used as the thermochemical standard (ΔH_h = −30.25 kcal/mol). Ethyl vinyl ether (99%), dihydropyran (99+%), 3,4-dihydro-2-methoxy-2*H*-pyran (99%), 5,6-dihydro-4-methoxy-2*H*-pyran (98%), 2,5-dimethoxy-2,5-dihydrofuran (99%), and 3-oxacyclopentene (97%) were obtained from Aldrich Chemical Co. Technical-grade 4-oxacyclopentene was obtained from Chemical Samples Co. Both oxacyclopentenes were dried by refluxing with sodium and then distilled from lithium aluminum hydride prior to hydrogenation, and both samples were homogeneous to GLC using a 100-ft SE-30 capillary column. 1,4-Bis(vinyloxy)butane and bis(vinyloxy) ethyl ether were obtained from General Aniline and Film Co. and were subjected to atmospheric distillation, with 0.1% hydroquinone added, prior to use.

As indicated in Table I, several solutions of ethers in hexane showed slight turbidity. The appearance of turbidity upon addition of a nonpolar solvent to an organic solute containing trace amounts of water is a complicated function of the miscibility of solute in solvent, the ratio of solute to solvent and the temperature.[11] We have used displacement of the cloud point of a solute–solvent system by trace amounts of water in the solute as an analytical method which is sensitive, under optimum conditions, to 0.06% water.[11] Conditions that obtain in mixing a hydrogenation sample with *n*-hexane as are dictated by the procedure used here are hardly optimum conditions for an analytical determination but it is reasonable to suppose that appearance of turbidity can be brought about by a very small amount of water in the ether–hexane solutions used for hydrogenation.

Experiments showed this to be so. A solution of 3-oxacyclopentene was purified by methods given above so that it gave a clear 10% solution with hexane. A 300-μL aliquot was intentionally contaminated with 0.5 μL of water (0.17%). The result, after stirring, appeared clear but had nearly microscopic droplets of water suspended in the ether, suggesting a saturated solution. Addition of 2 mL of hexane brought about distinct turbidity.

Procedure. The procedure was not different from what has been described[4] except that some interference was observed at the beginning of each set of experimental runs, probably from adsorption of the polar ether onto the catalyst support. We have previously noticed this effect upon hyrogenating esters[12] and

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[10] N. L. Allinger and Y. Yuh, *QCPE*, **12**, 395 (1980).

[11] D. W. Rogers and J. Scher, *Talanta*, **16**, 1579 (1969).

[12] D. W. Rogers and N. A. Siddiqui, *J. Phys. Chem.*, **79**, 574 (1975).

acids.[13] The first few injections of ether gave abnormally high results which we take to be the sum of the heat of hydrogenation plus the heat of adsorption of the product ether. The effect rapidly decreases and after 5 or 6 injections; a constant heat output is observed for the remainder of the experiment. We ascribe this to saturation of the adsorbant surface following which true heats of hydrogenation are obtained uncomplicated by interfering adsorption effects. The magnitude and sign of the early interference effects (2–5 kcal/mol and exothermic) are consistent with heats of fairly strong adsorption on activated charcoal.[14] No inconsistencies are observed in data sets from which the first 5 or 6 ether injections have been discarded.

9-Oxabicyclo[3.3.1]non-1-ene. The alkene was prepared from 1-hydroxy-9-oxabicyclo[3.3.1]nonane via the methanesulfonate, following the procedure of ref 15. The methanesulfonate; mp 75 °C, was recrystallized from benzene–ethyl acetate (lit.[15] mp 75 °C dec). Elimination with 2,6-di-*tert*-butylphenoxide gave the alkene, bp 67 °C (24 torr) [lit.[15] bp 67 °C (20 torr)].

Acknowledgment. We acknowledge support of this work by the National Institutes of Health.

Registry No. 1, 109-92-2; **2**, 3891-33-6; **3**, 764-99-8; **4**, 110-87-2; **5**, 4454-05-1; **6**, 17327-22-9; **7**, 40164-27-0; **8**, 1191-99-7; **9**, 1708-29-8; **10**, 332-77-4; 1-hydroxy-9-oxabicyclo[3.3.1]nonane, 37996-41-1; 1-hydroxy-9-oxabicyclo[3.3.1]nonanemethanesulfonate, 40164-33-8.

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(13) D. W. Rogers, O. P. A. Hoyte, and R. K. C. Ho, *J. Chem. Soc., Faraday Trans. 1*, 74, 46 (1978).

(14) A. W. Adamson, "Physical Chemistry of Surfaces", 2nd ed., Interscience, New York, 1967, p 402 ff.

(15) C. B. Quinn, Ph.D. Thesis, University of Michigan, 1973, pp 159, 164.

Linear Solvation Energy Relationships. 7. Correlations between the Solvent-Donicity and Acceptor-Number Scales and the Solvatochromic Parameters π^*, α, and β

R. W. Taft,* Norbert J. Pienta, Mortimer J. Kamlet,* and Edward M. Arnett

Department of Chemistry, University of California, Irvine, California 92717, the Department of Chemistry, University of Pittsburgh, Pittsburgh, Pennsylvania 15620, and the Naval Surface Weapons Center, White Oak Laboratory, Silver Spring, Maryland 20910

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The solvatochromic comparison method is used to examine relationships between Gutmann's solvent donicity (DN; based on ΔH_f of $SbCl_5$ complexes) and acceptor number (AN; based on ^{31}P NMR solvent shifts of Et_3PO) and the solvatochromic parameters π^*, α, and β. It is shown that the AN for nonprotonic solvents correlates well with π^* and for protonic solvents with a linear combination of π^* and α. It is therefore concluded that AN, represented as a measure of the solvent's ability to serve as an electron-pair acceptor, is, in fact, a combined measure of solvent polarity/polarizability and hydrogen bond donor ability. It is shown that DN is linear with β for oxygen bases and RCN nitrogen bases but that the correlation breaks down for pyridine. The breakdown in correlation is related to the nonlinearity between ΔH_f and ΔG_f of 4-fluorophenol complexes with HBA bases.

In earlier papers of this series,[1] we described the formulation of three scales of solvent properties (solvatochromic parameters)[2] which were used to unravel and rationalize medium effects on many types of reactivity parameters and physicochemical properties. A π^* scale of polarity/polarizabilities describes the solvent's ability to stabilize a charge or a dipole by virtue of its dielectric effect;[3] for most monofunctional aliphatic solvents, π^* values have been shown to be generally proportional to molecular dipole moments.[1,4,5] The α index of HBD (hydrogen bond donor) acidities provides a measure of the solvent's ability to donate a proton. We term this a "type-A hydrogen bond".[1,6] The β scale of HBA (hydrogen bond acceptor) basicities quantifies the solvent's ability to donate an electron pair (accept a proton). We call this participation in a type-B hydrogen bond.[1,7] Thus the terms A and B refer to the role of the solvent rather than to any major dichotomy of hydrogen bonds.

When hydrogen bonding effects are excluded, as when neither solutes nor solvents are hydrogen bond donors, correlations of medium effects with the solvatochromic parameters may take either of two forms. (1) For $p \rightarrow \pi^*$ or $\pi \rightarrow \pi^*$ electronic spectral transitions with all solvents considered together and for other properties or reactivity parameters XYZ (see below) when families of solvents with similar polarizability characteristics[4,5] are treated separately (e.g., only nonchlorinated aliphatic solvents, only polychlorinated aliphatics, or only aromatic solvents), the linear solvation energy relationships (LSER's) take the form of eq 1a, where s is a measure of the response of XYZ

$$\mathrm{XYZ} = \mathrm{XYZ}_0 + s\pi^* \tag{1a}$$

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* To whom correspondence should be addressed: R.W.T., University of California; M.J.K., Naval Surface Weapons Center.

(1) Earlier work is summarized in: Kamlet, M. J.; Abboud, J.-L. M.; Taft, R. W. *Prog. Phys. Org. Chem.* **1980**, *13*, 485.

(2) Although eq 1–3 have been extended to cover many nonspectroscopic properties, we find it convenient to continue to refer to the method as the solvatochromic comparison method, the equations as the solvatochromic equations, the π^*, α, β, and δ terms as the solvatochromic parameters, and the s, a, b and d terms as the solvatochromic coefficients.

(3) (a) Kamlet, M. J.; Abboud, J.-L. M.; Taft, R. W. *J. Am. Chem. Soc.* **1977**, *99*, 6027. (b) Kamlet, M. J.; Hall, T. N.; Boykin, J.; Taft, R. W. *J. Org. Chem.* **1979**, *44*, 2599.

(4) Abboud, J.-L. M.; Kamlet, M. J.; Taft, R. W. *J. Am. Chem. Soc.* **1977**, *99*, 8325.

(5) Abboud, J.-L. M.; Taft, R. W. *J. Phys. Chem.* **1979**, *83*, 412.

(6) (a) Kamlet, M. J.; Taft, R. W. *J. Chem. Soc., Perkin Trans. 2* **1979**, 349. (b) Taft, R. W.; Kamlet, M. J. *Ibid.* **1979**, 1723.

(7) (a) Kamlet, M. J.; Taft, R. W. *J. Am. Chem. Soc.* **1976**, *98*, 377. (b) Yokoyama, T.; Taft, R. W.; Kamlet, M. J. *Ibid.* **1976**, *98*, 3233. (c) Kamlet, M. J.; Solomonovici, A.; Taft, R. W. *Ibid.* **1979**, *101*, 3734. (d) Kamlet, M. J.; Jones, M. E.; Taft, R. W.; Abboud, J.-L. M. *J. Chem. Soc., Perkin Trans. 2* **1979**, 342.

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