

highly unstable species. Quite analogous results have been obtained from π -route studies by Peterson and Kamat.⁶ The only cyclized products from 6-heptyn-2-yl tosylate, a terminal acetylene, were six-membered rings. In contrast, solvolysis of 6-octyn-2-yl tosylate gave both five- and six-membered ring products in ratios rather similar to those found here from III, despite the different solvents which were employed in the two studies.

Despite the nonlinear nature of the vinyl cation in IX, these product results indicate that IX and X do not differ much in stability. This is to be expected, since methylenecyclopentane (a model for X) is nearly 5 kcal/mol (enthalpy) less stable due to ring strain than is 1-methylcyclohexene (a model for IX).¹⁰ The $10^{-3.5}$ rate depression observed for II corresponds to an activation free-energy difference of 6 kcal/mol. Thus, ring strain and vinyl cation strain factors seem to balance in IX and X.

For this reason, it is difficult to attribute the tenfold rate enhancement of III over II to anchimeric assistance during rearrangement of IX to X. The rate enhancements in IV and V are an additional order of magnitude larger, but little rearranged product is found from VI. In short, rearrangements to more stable cations do not seem to provide driving force for the rate enhancements observed in Table III.

The situation is even more telling with V, which shows the largest rate enhancement, nearly 10^3 over II. Neither possible mode of ring contraction is observed; instead, the majority of products (but not all) form by methyl shift. Since the methyl groups cannot possibly be oriented at the backside of the departing triflate group, participation in this instance seems highly unlikely.

The rate enhancements observed for substituted compounds in 50% EtOH at 100° thus appear to be due to three possible causes: (1) formation of bridged ions more stable than their classical counterparts⁶ (however, molecular orbital calculations do not support this possibility,¹ except, perhaps, for the smallest ring systems not considered in the present paper¹¹); (2) inductive and hyperconjugative substituent effects of unusually large magnitude;¹² (3) relief of steric ground-state interactions between the substituents and the triflate leaving groups during solvolysis.¹³ The detailed interpretation of the rate enhancements of substituted compounds, e.g., III–VI, is under active investigation.

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Dispersion Force Contribution to Heats of Protonation^{1,2}

Sir:

On comparing heats of protonation of homologous primary alcohols and amines referred to a gaseous reference state, we find a trend which is evidently due to a systematic contribution of dispersion or London forces.³ Except for cases such as the ionization of neutral molecules to form large delocalized (polarizable) ions or transition states⁴ in solution the effects of these forces are nearly equivalent in both the secondary and the initial states so that their presence is not normally brought to our attention.

Table I contains heats of solution of six primary alcohols and three primary amines in fluorosulfuric acid as well as $\Delta\bar{H}_s$ values for two of the amines in 96.5% H₂SO₄. Heats of transfer from the gas phase to high dilution in HSO₃F or H₂SO₄ (in which all the compounds are completely protonated⁵) are calculated by subtracting $\Delta\bar{H}_{vap}$ from $\Delta\bar{H}_s$ and are found in columns III and VIII. It is evident that the enthalpy of transfer of alcohols and amines from the gas state to solution in strong acid becomes more exothermic in direct proportion to the carbon number of the alkyl chain.

The stability of the protonated solutes in HSO₃F was shown in two ways. (a) Clean, easily interpreted nmr spectra were obtained at -60° for the alcohols. As previous workers have observed,⁶ the protons on

(1) Solvent Effects in Organic Chemistry. XII.

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(3) These self-induced attractions result from the interaction of instantaneous dipoles produced by zero-point motions within molecules or parts of molecules. They occur between all types of matter, provided the distance separating the interacting pairs is large enough to make electron exchange negligible, and are sometimes the major contribution to van der Waals forces in liquids.

(4) E. Grunwald and E. Price, *J. Amer. Chem. Soc.*, **86**, 4517 (1964).

(5) E. M. Arnett, J. J. Burke, and R. P. Quirk, *ibid.*, **92**, 1260 (1970), estimate a value of -5.1 for the pK_{BH^+} of ethanol based on their enthalpic basicity scale. Since increasing the chain length has a negligible effect on the basicity of the aliphatic alcohols, HSO₃F, with an H_0 of -13.9, can be expected to protonate these alcohols completely.

(6) T. Birchall and R. J. Gillespie, *Can. J. Chem.*, **43**, 1045 (1965), record the nmr spectrum of EtOH in HSO₃F at 25, -82, and -95°. At 25° they note only CH₂ and CH₃ resonances, while at the lower temperatures a new peak appears at about -10 ppm from external TMS. They attribute this peak to the -OH₂⁺ protons. Evidently at -60°, the temperature at which our spectra were recorded, exchange with the solvent is still too fast for the -OH₂⁺ resonance to be observed. Alternatively, noting the temperature dependence of the -OH₂⁺ peak observed by Birchall and Gillespie ($\Delta = -9.89$ ppm at -95°, -10.35 ppm at -82°), it is possible that at -60° the -OH₂⁺ resonance is close enough to the solvent peak to be swamped by it.

(10) P. v. R. Schleyer, J. E. Williams, and K. R. Blanchard, *J. Amer. Chem. Soc.*, **92**, 2377 (1970).

(11) H. Fischer, K. Hummel, and M. Hanack, *Tetrahedron Lett.*, 2169 (1969); H. Fischer and H. Kollmar, *Theor. Chim. Acta*, **16**, 163 (1970).

(12) Compare the behavior of secondary alkyl tosylates in trifluoroacetic acid: P. E. Peterson, R. E. Kelly, Jr., R. Belloli, and K. A. Sipp, *J. Amer. Chem. Soc.*, **87**, 5169 (1965).

(13) The suggestion of a referee. Also see footnote 10a in J. L. Fry, J. M. Harris, R. C. Bingham, and P. v. R. Schleyer, *ibid.*, **92**, 2540 (1970), and footnote 20a in J. L. Fry, C. J. Lancelot, L. K. M. Lam, J. M. Harris, R. C. Bingham, D. J. Raber, R. E. Hall, and P. v. R. Schleyer, *ibid.*, **92**, 2538 (1970).

Table I. Heats of Transfer from the Gas Phase to Solution in HSO₃F or 96.5% H₂SO₄ of Several Aliphatic Alcohols and Amines

Compound	I	II		III	IV	V	VI	VII	VIII	IX
	$-\Delta\bar{H}_{\text{HSO}_3\text{F}}$, (temp, °C)	$-\Delta\bar{H}_{\text{a,b}}$ ^c	$-\Delta\bar{H}_{\text{t,g} \rightarrow \text{HSO}_3\text{F}}$ ^a	Δ^b		$-\Delta\bar{H}_{\text{cond}}$ (-50) RCH ₃	Δ^b	$-\Delta\bar{H}_{\text{H}_2\text{SO}_4}$ (temp, °C)	$-\Delta\bar{H}_{\text{t,g} \rightarrow \text{H}_2\text{SO}_4}$ ^a	Δ^b
Methanol	14.3 ± 0.5 (-52)	19.6 ± 0.6	22.7		2.1	3.38	1.2			
Ethanol	15.3 ± 0.4 (-48)	20.2 ± 0.5	24.8		1.7	4.55	1.1			
Propanol	15.7 ± 1.1 (-53)		26.5		2.1	5.61				
Butanol	16.6 ± 0.4 (-54)		28.6		1.1					
Pentanol	16.3 ± 0.3 (-50)		29.7		1.4					
Hexanol	16.3 ± 0.4 (-43)	21.0 ± 0.5	31.1							
Propylamine	45.4 ± 0.7 (27)		52.8		2.7			38.4 ± 0.7 (26)	45.8	
Pentylamine	45.9 ± 0.2 (25)		55.5		3.5			38.4 ± 1.1 (28)	48.0	2.2
Octylamine	46.1 ± 0.4 (29)		59.0							

^a Heats of transfer are obtained by subtracting the heat of vaporization from the heat of solution found in columns I and III. The $\Delta\bar{H}_{\text{vap}}$ values for the alcohols were calculated from the relation $\Delta\bar{H}_{\text{vap}}(T, ^\circ\text{C}) = \Delta\bar{H}_{\text{vap}}(25^\circ) + (C_p^{\text{v}} - C_p^{\text{l}})/\Delta T$. $\Delta\bar{H}_{\text{vap}}(25^\circ)$ values were taken from C. V. Krishnan and H. L. Friedman, *J. Phys. Chem.*, **73**, 1572 (1969), C_p^{v} and C_p^{l} (except for 1-hexanol) values from E. M. Arnett, W. B. Kover, and J. V. Carter, *J. Amer. Chem. Soc.*, **91**, 4028 (1969). For 1-hexanol C_p^{l} was from Landolt-Bornstein, while C_p^{v} was obtained by extrapolating a plot of C_p^{v} vs. carbon number for the other five normal alcohols. Values in column II are calculated as $\Delta\bar{H}_{\text{a,b}} = \Delta\bar{H}_{\text{HSO}_3\text{F}}(-50^\circ) - \Delta\bar{H}_{\text{CCl}_4}(-20^\circ)$. Since CCl₄ freezes at -22.6°, heats could not be measured in both solvents at -50° so $\Delta\bar{H}_{\text{a,b}}$ is not exactly equivalent to $\Delta\bar{H}_{\text{a,b}}$ in ref 3. ^b Δ values represent the differences between the numbers above and below to the left in the preceding columns.

oxygen could not be resolved owing to rapid exchange with solvent, but the alkyl portion of each alcohol gave a clearly defined α -methylene resonance shifted well downfield, a methyl signal, and a multiplet for the intervening methylene hydrogens. Each spectrum gave the proper integration. (b) Immediate and complete evolution of heat resulted from addition of the solute to the acid at the indicated temperature.⁷

The observed trend of increasing exothermicity with increasing chain length⁸ cannot be due to an inductive effect, since the effect of increasing the alkyl chain on stabilizing the resulting ion should drop off rapidly.⁹

On the other hand, it is reasonable both from qualitative and quantitative considerations that the observed differences in $\Delta\bar{H}_{\text{t}}$ within both series are a manifestation of increasingly large dispersion force interactions (for solvation of a homologous series in a common solvent) as the hydrocarbon chain length is progressively increased. Transfer of a solute from the gas phase (where (within the present context) attractive forces of all types are negligible) to high dilution in a solvent is a process in which dispersion forces must be a factor: they are not present in the gaseous initial state but make their full contribution to the condensed secondary state. For example, differences in $\Delta\bar{H}_{\text{vap}}$ of paraffin hydrocarbons can be considered as differences in the dispersion energies of those hydrocarbons.¹⁰ It is instructive to compare the effect per CH₂ group on the heat of condensation ($\Delta\bar{H}_{\text{cond}}$) at -50° of the three hydrocarbons in column V of Table I

(7) The solution in the calorimeter was clear and water white at the end of each measurement at low temperature. On warming to room temperature, the solutions became dark with the exception of the solutions of methanol and ethanol, which are stable at room temperature.

(8) The energy of cavity formation in the solvent should show a regular endothermic increase (for transfer from the gas phase to solution) as the size of the alkyl group increases.

(9) (a) W. A. Waters, *J. Chem. Soc.*, 1551 (1933); (b) R. W. Taft, Jr., in "Steric Effects in Organic Chemistry," M. S. Newman, Ed., Wiley, New York, N. Y., 1956, p 592.

(10) B. Linder, *J. Chem. Phys.*, **33**, 668 (1960).

with the same effect on $\Delta\bar{H}_{\text{t,g} \rightarrow \text{acid}}$ (columns III and VIII).

The magnitude of the dispersion interaction between two molecules depends upon the number and strength of their centers of dispersion (or monopoles¹¹). Thus, in the interaction of a homologous series of compounds with a single solvent, there will be a regular incremental increase in the number of dispersion centers for each higher homolog, resulting in an accompanying regular increase in the attractive force due to dispersion. In the analysis of data for a short series of homologs, such a substituent effect could easily be confused with alkyl inductive effects.

If we assume that the energy term for protonation of the hydroxy (or amino) group is the same for all of these alcohols (or amines), *i.e.*, that the basicities of the normal alcohols and amines are not much affected by chain length, the energy differences observed in the transfer of both series of compounds from the gas phase to solution in fluorosulfuric acid are of the correct magnitude to be accounted for as a dispersion effect. (This assumption is supported by the constancy of the values in Table I for $\Delta\bar{H}_{\text{a,b}}$, a criterion of base strength.¹²)

Although the necessary data are not available to calculate dispersion energies between HSO₃F and other molecules, it is possible to make such calculations on another system for which we do have calorimetric data, alcohols as solutes in CCl₄. The following form of London's approximation¹³

$$E_{\text{disp}} = -\frac{\alpha_a \alpha_b}{R_{\text{ab}}^6} \frac{3I_a I_b}{2(I_a + I_b)} \quad (1)$$

in which α = polarizability in cubic ångströms, I = ionization potential,¹⁴ and R = distance between interacting

(11) F. London, *J. Phys. Chem.*, **46**, 305 (1942).

(12) $\Delta\bar{H}_{\text{a,b}} = \Delta\bar{H}_{\text{HSO}_3\text{F}} - \Delta\bar{H}_{\text{CCl}_4}$ (ref 1).

(13) F. London, *Trans. Faraday Soc.*, **33**, 8 (1937).

Table II. Heats of Transfer of Alcohols from the Gas Phase to Solution in CCl₄ at 25°. Calculated Dispersion Force Interactions

Compound	I	II	Δ^b	III	IV		Δ^b
	$\Delta\bar{H}_{\text{CCl}_4}$, kcal/mol	$\Delta\bar{H}_{\text{t,g}\rightarrow\text{CCl}_4}$, kcal/mol		Eq 1 ^a	$-E_{\text{disp}}$, kcal/mol ($R = 4 \text{ \AA}$)	Eq 2 ^a	
Methanol	4.36	4.71		2.0		6.0	
Ethanol	4.49	5.69	1.0	2.9	.9	+10.0	4.0
Propanol	4.20	7.16	1.5	3.8	.9	13.5	3.5
Butanol	4.04	8.58	1.4	4.8	1.0	16.4	3.0

^a Calculated using $R = 4 \text{ \AA}$. ^b Δ values represent the differences between the numbers above and below to the left in the preceding columns.

centers in ångströms, gives values found in column III of Table II for the attractive force due to dispersion interaction between CCl₄ and each of four primary alcohols, when $R = 4 \text{ \AA}$. Using an approximation suggested by Linder¹⁰ and Grunwald and Ralph¹⁵

$$E_{\text{disp}} = 6.69 \times 10^{-33} \frac{\chi_a \chi_b}{(\nu_a + \nu_b) R_{ab}^6} \quad (2)$$

in which χ = diamagnetic susceptibility and $h\nu$ is represented as the ionization potential (h is contained in the constant), values shown in column IV of Table II are calculated for the same interactions. The experimental values with which to compare the entries in columns III and IV are the heats of transfer from the gas phase to high dilution in CCl₄, found by subtracting the heat of vaporization of a particular alcohol from its heat of solution in CCl₄. Comparing these heats of transfer, found in column II, with the calculated dispersion energies, one sees that the calculations give values which are in the correct order and are of the proper magnitude to account for the interactions between these alcohols and CCl₄. With the chosen value of R , eq 1 slightly underestimates the magnitude of the effect while eq 2 overestimates it. Examination of the differences between $\Delta\bar{H}_{\text{t,g}\rightarrow\text{CCl}_4}$ for any two of the alcohols in Table II which differ by only one methylene group shows that the CCl₄-methylene interaction is worth from 1 to 1.5 kcal/mol, as shown by the values in the columns labeled Δ . The calculated dispersion energies yield values of about 1 kcal/mol (when the London equation is used) to 3–4 kcal/mol (using the Linder equation) for the same interaction when obtained by difference as shown in the columns labeled Δ in Table II.¹⁶ A direct calculation of this interaction using eq 1 with $R = 4 \text{ \AA}$ and 10.4^{14} for the ionization potential of CH₂ yields -0.95 kcal/mol. Thus the differences in $\Delta\bar{H}_{\text{t}}$ as well as the actual values in the case of CCl₄ as solvent can be accounted for by dispersion interactions between solute and solvent.

It thus appears reasonable to ascribe the trends evidenced in both heats of protonation in strong acid

(14) Ionization potentials were taken from J. L. Franklin, J. G. Dillard, H. M. Rosenstock, J. T. Herron, K. Droxil, and F. H. Field, "Ionization Potentials, Appearance Potentials, and Heats of Formation of Gaseous Positive Ions," NSRDS-NBS No. 26, U. S. Government Printing Office, Washington, D. C.,

(15) E. Grunwald and E. K. Ralph, III, *J. Amer. Chem. Soc.*, **89**, 4405 (1967).

(16) Grunwald and Ralph¹⁵ find that the substituent effect on R_H , the rate constant for the breakage of the $R_3N \cdot HOH$ hydrogen bond, is of the same magnitude as the London dispersion interaction between the water molecule and the R groups. A plot of $\delta_R F_{\text{disp}}$ vs. $-RT \delta_R \ln R_H$ gives different lines depending upon whether eq 1 or 2 is used to calculate $\delta_R F_{\text{disp}}$. Equation 1 gives a lower estimate of $\delta_R F_{\text{disp}}$ than does eq 2, while a line of unit slope falls between the two.

and heats of solution in CCl₄ of these primary alcohols and amines, from the common gaseous reference state, to dispersion interactions between solvent molecules and the alkyl chains of the solute molecules.

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Homoconjugational Ionization Reaction of Anhydrous Perchloric Acid in Dichloromethane

Sir:

While acid-base reactions have been investigated in aprotic solvents of low dielectric constants such as hydrocarbons and alkyl halides,^{1,2} little has been reported on such reactions in dichloromethane.

In the course of our studies devoted to electrochemical reactions in the latter solvent, we have previously defined its electroactivity range on platinum, mercury, and silver electrodes and described the properties of the Ag|Ag₃I₄⁻, N(*n*-C₄H₉)₄⁺ system which provided a suitable reference electrode.³

We are presently investigating in dichloromethane acid-base reactions which frequently determine the paths and kinetics of electrochemical reactions. We have developed and tested a glass electrode filled with dichloromethane for titration of halides and amines by anhydrous perchloric acid solutions in dichloromethane.⁴

In this paper, evidence of the homoconjugation of anhydrous perchloric acid in dichloromethane solutions is presented. This homoconjugation (and dimerization of perchloric acid) can be attributed to the weak hydrogen bond donating and accepting properties of the solvent. Gandini and Plesch⁵ have already stated that a four-molecule association of the acid is consistent with the kinetics of styrene protonation in this solvent; they reported a specific electrical conductivity of $9 \times 10^{-8} \text{ ohm}^{-1} \text{ cm}^{-1}$ for a 0.04 *M* solution which demonstrates the very low degree of dissociation of the

(1) G. Charlot and B. Tremillon, "Chemical Reactions in Solvents and Melts," Pergamon Press, Elmsford, N. Y., 1969.

(2) J. F. Coetzee and C. D. Ritchie, Ed., "Solute Solvent Interactions," Marcel Dekker, New York, N. Y., 1969.

(3) D. M. Coutagne, *Bull. Soc. Chim. Fr.*, in press.

(4) D. M. Coutagne, unpublished results.

(5) A. Gandini and P. H. Plesch, *J. Chem. Soc.*, 4765, 6019 (1965); 7 (1966); *Eur. Polym. J.*, **4**, 55 (1968).