Table II. Heats of Transfer of Alcohols from the Gas Phase to Solution in CCl_4 at 25°. Calculated Dispersion Force Interactions

	I	II		III		IV	
				$-E_{disp}$, kcal/mol (R = 4 Å)			
Compound	$\Delta\bar{H}_{CCl_4}$, kcal/mol	$\Delta\bar{H}_{t,g\rightarrow CCl_4}$, kcal/mol	Δ[b]	Eq 1[a]	Δ[b]	Eq 2[a]	Δ[b]
Methanol	4.36	4.71		2.0		6.0	
			1.0		.9		4.0
Ethanol	4.49	5.69		2.9		+10.0	
			1.5		.9		3.5
Propanol	4.20	7.16		3.8		13.5	
			1.4		1.0		3.0
Butanol	4.04	8.58		4.8		16.4	

[a] Calculated using R = 4 Å. [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 CCl_4 and each of four primary alcohols, when R = 4 Å. Using an approximation suggested by Linder[10] and Grunwald and Ralph[15]

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

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 CCl_4, found by subtracting the heat of vaporization of a particular alcohol from its heat of solution in CCl_4. 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 CCl_4. 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 $\Delta\bar{H}_{t,g\rightarrow CCl_4}$ for any two of the alcohols in Table II which differ by only one methylene group shows that the CCl_4–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 Å and 10.4[14] for the ionization potential of CH_2 yields −0.95 kcal/mol. Thus the differences in $\Delta\bar{H}_t$ as well as the actual values in the case of CCl_4 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 and heats of solution in CCl_4 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.

Acknowledgment. We are pleased to acknowledge the assistance of Mr. Timothy R. Drury in carrying out the experiments.

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Received October 12, 1970

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[14] Ionization potentials were taken from J. L. Franklin, J. G. Dillard, H. M. Rosenstock, J. T. Herron, K. Droxl, 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 Ralph[15] 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 $\delta_R F_{disp}$ *vs.* $-RT\ \delta_R \ln R_H$ gives different lines depending upon whether eq 1 or 2 is used to calculate $\delta_R F_{disp}$. Equation 1 gives a lower estimate of $\delta_R F_{disp}$ than does eq 2, while a line of unit slope falls between the two.

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 $Ag|Ag_3I_4^-,N(n\text{-}C_4H_9)_4^+$ 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 Plesch[5] 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 9×10^{-8} ohm^{-1} cm^{-1} for a 0.04 M solution which demonstrates the very low degree of dissociation of the

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[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).

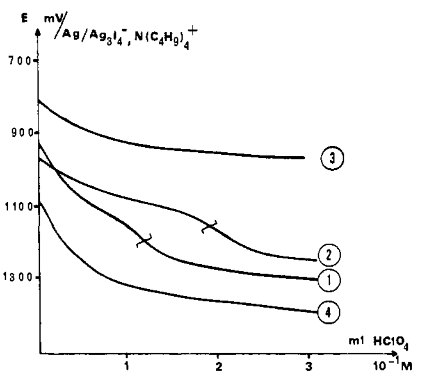


Figure 1. Glass electrode measurement in dichloromethane titration of 10 ml of tetrabutylammonium perchlorate (TBAP) solution by anhydrous perchloric acid: (1) TBAP 1.2×10^{-2} *M*, (2) TBAP 1.8×10^{-2} *M*, (3) TBAP 0.5 *M*, (4) pure CH_2Cl_2.

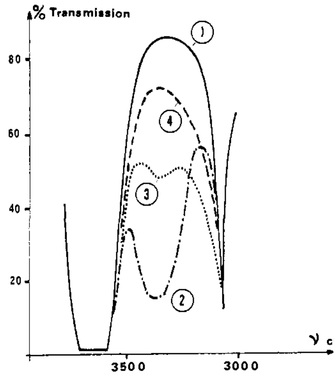


Figure 2. Infrared spectroscopic characterization of the anhydrous perchloric acid OH bonding alteration when $H(ClO_4)_2^-,N(n\text{-}C_4H_9)_4^+$ is formed in dichloromethane: (1) pure CH_2Cl_2; (2) $HClO_4$ 1 *M*; (3) $HClO_4$ 1 *M*, TBAP 0.3 *M*; (4) $HClO_4$ 1 *M*, TBAP 1 *M*.

anhydrous perchloric acid. We also believe that in dichloromethane, in which hydroxonium perchlorate is insoluble, the following reaction proposed by Bout and Potier[6] in pure anhydrous perchloric acid

$$3HClO_4 \rightleftharpoons Cl_2O_7 + H_3O^+ + ClO_4^-$$

does not occur or proceeds very slowly because of the high stability of 1 *M* anhydrous perchloric acid solutions saturated with monohydrate.

Properties of Brønsted acid HA in aprotic solvents (S) of low dielectric constants are determined by a two-step equilibrium reaction, which involves (1) the ionization of the molecule into an ion pair and (2) the dissociation of this ion pair.[7]

$$HA + S \rightleftharpoons (H^+,A^-)_S \rightleftharpoons H_S^+ + A^-$$

Our results are better interpreted if it is assumed that dimerization of anhydrous perchloric acid can take place in dichloromethane according to the equilibrium reaction $2HClO_4 \rightleftharpoons (HClO_4)_2$. Acid–base properties of perchloric acid solutions would then depend on the following successive equilibria.

$$HClO_4 + S \rightleftharpoons (H^+,ClO_4^-)_S \rightleftharpoons H_S^+ + ClO_4^-$$

$$(HClO_4)_2 + S \rightleftharpoons (H^+,H(ClO_4)_2^-)_S \rightleftharpoons H_S^+ + H(ClO_4)_2^-$$

$$H(ClO_4)_2^- + S \rightleftharpoons (H^+,2ClO_4^-)_S \rightleftharpoons H_S^+ + 2ClO_4^-$$

The formation of the ion pair $H^+,H(ClO_4)_2^-$ and the existence of the homoconjugate ion $H(ClO_4)_2^-$ can be compared with the homoconjugation of mineral acids in acetonitrile detected by Kolthoff, *et al.*[8] The dimer of perchloric acid should be considered as a diacid; if the strengths of its two acidic functions are sufficiently different, we expect the base $N(n\text{-}C_4H_9)_4^+ClO_4^-$ to react with the acids $HClO_4$ and $(HClO_4)_2$ according to the following reactions.

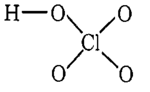
$$H^+ClO_4^- + N(n\text{-}C_4H_9)_4^+ClO_4^- \rightleftharpoons H(ClO_4)_2^-N(n\text{-}C_4H_9)_4^+ \quad (I)$$

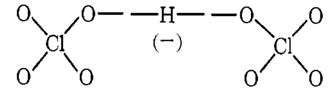
$$H^+H(ClO_4)_2^- + 2N(n\text{-}C_4H_9)_4^+ClO_4^- \rightleftharpoons 2H(ClO_4)_2^-N(n\text{-}C_4H_9)_4^+ \quad (II)$$

Potentiometric measurements and infrared spectrophotometry[9] give evidence that these reactions occur effectively and reach completion. For the preparation of anhydrous perchloric acid, we used the method described by Mascherpa.[10]

It is possible to follow with a glass indicator electrode the titration of tetrabutylammonium perchlorate in dichloromethane by 0.1 *M* anhydrous perchloric acid in the same solvent. Figure 1 (curves 1 and 2) shows that one molecule of perchlorate combines with one molecule of perchloric acid. Consequently, an excess of tetrabutylammonium perchlorate lowers the strength of perchloric acid, as is shown by curves 3 and 4 in Figure 1.

Infrared spectrophotometry shows a complete alteration of the OH bonding of perchloric acid when a stoichiometric equivalent of tetrabutylammonium perchlorate is added to a perchloric acid solution in CH_2Cl_2 (Figure 2). This is indicated by the disappearance of the OH absorption band at 3350 cm^{-1}. Such an effect is expected if the structures of perchloric acid and its "complex" with perchlorate are described by models A and B.


A


B

The latter results give further evidence that reactions I and II are strongly shifted to the right.

We have already mentioned the strong affinity of water for anhydrous perchloric acid; this is illustrated by the fact that when in contact with atmospheric moisture, its solution in dichloromethane fumes and yields white hydroxonium perchlorate crystals according to the reaction

$$HClO_4 + H_2O \rightleftharpoons H_3O^+ClO_4^-\downarrow$$

On the contrary, no reaction with water takes place when an excess of tetrabutylammonium perchlorate is present; an addition of this perchlorate instantaneously dissolves hydroxonium perchlorate crystals as the following reaction takes place

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(6) N. Bout and J. Potier, *Rev. Chim. Miner.*, **4**, 621 (1967).

(7) No hypothesis is made about the eventual solvation of the anion A^-.

(8) J. M. Kolthoff, S. Bruckenstein, and M. K. Chantooni, *J. Amer. Chem. Soc.*, **83**, 3927 (1961).

(9) Potentiometric measurements are made with the $Ag|Ag_3I_4^-,N(n\text{-}C_4H_9)_4^+$ reference electrode,[3] the glass indicator electrode,[4] and an EPL 1 Tacussel Solea recording potentiometer. Infrared spectra are recorded on a Perkin-Elmer 337 spectrophotometer using a 0.1-mm silica cell.

(10) G. Mascherpa, *C. R. Acad. Sci.*, **252**, 1800 (1961). Contact with atmospheric moisture is avoided by directly transferring the collected anhydrous perchloric acid into a flask containing carefully dried and purified dichloromethane.[8]

$$H_3O^+ClO_4^- \downarrow + N(n\text{-}C_4H_9)_4{}^+ClO_4^- \longrightarrow H_2O + N(n\text{-}C_4H_9)_4{}^+H(ClO_4)_2^-$$

In terms of acid–base reactions, we conclude that water in dichloromethane is a weaker base with respect to perchloric acid than tetrabutylammonium perchlorate. For electrochemical studies in dichloromethane, we must consider that the strength of the perchloric acid is weakened in the presence of tetrabutylammonium perchlorate when this salt is used as supporting electrolyte.

Acknowledgment. We are grateful to Professor G. Cauquis of Grenoble University, and to Dr. S. Deron for advice and discussions.

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Anomalous Features of Nuclear Magnetic Resonance Spectra of Methyl and Methylene Halides Oriented in a Nematic Solvent. Unusual Ordering due to Specific Solute–Solvent Interaction

Sir:

In the present communication we wish to report the observation of unusual ordering of the solute molecule arising from specific solute–solvent interaction in the nematic phase, where separation of the spectral splitting increases when temperature is raised. This finding is expected to shed light on the elucidation of the nature of ordering of the solute molecule in the liquid-crystal solvent.

We have measured proton magnetic resonance spectra of CH_3X (X = I, Br, and CN) and CH_2X_2 (X = I and Cl) dissolved in the various nematic solvents I–V; (I, *p,p'*-ethoxyphenylazophenyl valerate; II, *p,p'*-ethoxyphenylazophenyl hexanoate; III, the mixture of 40 mol % I and 60 mol % II; IV, *p,p'*-ethoxyphenylazophenyl heptanoate; and V, *p,p'*-di-*n*-hexyloxyazoxybenzene). Spectra were obtained at 60 MHz (Jeolco 3H-60) and at 220 MHz (Varian HR-220) at various temperatures ranging from 30 to 110°.

Figure 1 shows an example of proton nmr spectra of 10% methyl iodide in III at various temperatures. With increasing temperature, the spacing of the triplet signal increased gradually. When the temperature is raised more (near the nematic–isotropic transition), the separation decreased rapidly in a normal way, leading to the appearance of isotropic spectrum. These unusual phenomena were found to be reversible with respect to raising and lowering the temperature. The unusual temperature dependency of the spectral splitting for methyl iodide was encountered for solvents I–IV, but not for V. In the mixed solvent III, this anomalous behavior is most conspicuous. Figures 2 and 3 present the temperature dependence of the degree of order, S_{zz}, which describes the average orientation of the molecular threefold axis (*z* axis) with respect to the applied magnetic field for CH_3I, CH_3Br, and CH_3CN in solvents III and V, respectively. Methyl iodide has the maximum value of S_{zz} at an appreciably high temperature (85–90°) in solvent III. Acetonitrile behaves in an almost ordinary manner in all the solvents;[1] the S_{zz} value increases linearly with decreasing temperature, although at lower temperatures this temperature dependency deviates slightly from linearity. Methyl bromide behaves in a manner similar to methyl iodide: the spectral splitting maintained almost constant separation in solvent III when the temperature was varied from 30 to 110°. The results obtained by the usual 60-MHz nmr spectrometer were reproduced by 220-MHz nmr with rapid sample spinning. The unusual phenomena were not affected significantly by variation of solute concentration or by addition of tetramethylsilane, a globular molecule.

For methylene halides, similar unusual but not so conspicuous observations as for the methyl halides were obtained in solvent III. The doublet separation for methylene iodide in III (10 mol %) increases until the temperature is raised from 30 to 50°, but above this temperature the separation decreases gradually in a normal manner. When the temperature was lowered, this unusual spectral change was reproduced. Methylene chloride, however, exhibits a normal trend for all the solvents (see Figure 4).

From these observations it could be said that the unusual temperature dependency of the spectral splitting of the oriented solute molecule is characteristic of iodide or bromide derivatives dissolved in the nematic solvent of azo compounds I–IV. These observations allow us to expect that the specific solute–solvent interaction in the nematic phase is responsible for the unusual alignment of the solute molecule.[2] The unusual observations presented above are not absolutely due to temperature inhomogeneity in the nmr probe. This is confirmed from the facts that this phenomenon is reversible with raising or lowering temperature, that it is not significantly affected by the solute concentration, and that it is always reproduced in 60-MHz nmr with no spinning and in the 220-MHz nmr with rapid spinning of the sample tube. It seems also unlikely that a "looser" nematic phase is produced at the lower temperature in which the isotropic motion of the solute molecule is partially allowed, resulting in the decrease in the S_{zz} value. The following mechanism is proposed to explain how the unusual temperature dependence of the spectral splitting occurs. We are now forced to assume that methyl iodide does not remain in a single mode of orientation, but in at least two modes of orientation[3] which are in an equilibrium state and have opposite directions of ordering. Temperature variation shifts this equilibrium, thus leading to the change in the apparent S_{zz} value. The smaller spacing of the spectral splitting at lower temperature possibly implies that methyl iodide tends to be aligned

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[1] In order to substantiate further this unusual behavior, we measured ^{13}C nmr spectra of 50% enriched $^{13}CH_3I$ and $^{13}CH_3CN$ dissolved in solvent III at 15.1 MHz on a Jeolco 3H-60 spectrometer [for a detailed description of the ^{13}C nmr of oriented molecules in the nematic solvent, see I. Morishima, A. Mizuno, and T. Yonezawa, *Chem. Phys. Lett.*, 7, 633 (1970)]. The spectral splitting in the quartet pattern also exhibited unusual temperature dependency as in the proton nmr spectra for $^{13}CH_3I$ but not for $^{13}CH_3CN$.

[2] ^{13}C chemical shift of $^{13}CH_3I$ in solvent III is almost equal to that in the solvent V and in neat liquid, indicating that CH_3I does not exist as quaternary ion forming at nitrogen atom of the solvent molecule.

[3] Nonunique ordering of the solute molecule in liquid-crystal solvents has recently been detected by nmr [T. Yonezawa, I. Morishima, K. Deguchi, and H. Kato, *J. Chem. Phys.*, **51**, 5731 (1969)] and by epr [G. Havach, P. Ferruti, D. Gill, and M. P. Klein, *J. Amer. Chem. Soc.*, **91**, 7526 (1969)].