(18) An alternate explanation is that the 1,1-cycloaddition process occurs by initial attack of the carbene carbon onto the terminal position of the double bond. Such an attack will generate a six-membered ring dipole which contains a secondary carbonium ion as well as an azaallyl anion portion. Collapse of this new 1,3-dipole to the thermodynamically favored exo product will result in a severe torsional barrier on closure. On the other hand, collapse to the thermodynamically less favored endo isomer moves the phenyl and methyl groups increasingly further apart and could account for the formation of the less stable product. The major flaw with this rationale, however, is that initial bond formation should occur via a five-membered ring since the methyl group on the terminal position would be expected to stabilize the incipient carbonium ion generated. Further work with other terminally substituted olefins is in progress and should clarify this point.

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Pressure Effects on Conformational Equilibrium in Solution. Infrared Studies of Halocyclohexanes

Sir:

Present knowledge of the effects of pressure on chemical equilibrium is very limited. Inherently, such information would be valuable in improving our understanding of the properties of dissolved molecules; data from pressure studies could supplement the many important results obtained from investigations of solvent and temperature effects on chemical equilibrium. Since high pressure spectral techniques have been available for several decades,[1] it is surprising that there have been so few careful studies of solutions at high pressure. In particular, we can find no quantitative spectral investigations of conformational equilibria at increased pressures. A major reason for the scarcity of quantitative solution results is probably the difficulty of measuring pressures in compressed liquid samples.

Numerous compounds existing as mixtures of conformers have vibrational modes (fundamentals and combinations) for each conformer which give rise to distinct, well-separated bands in the infrared or Raman spectra. For example, many bands in the spectra of halocyclohexanes (in the 1500-100-cm^{-1} region) have been assigned to axial or equatorial forms.[2] Variations in temperature or solvent can induce changes in conformational equilibria, and quantitative intensity studies of certain vibrations have been used to infer changes in equilibrium constants.[3] We are at present using a related approach to investigate the effects of pressure on conformational equilibria and report here quantitative results for dilute solutions of chlorocyclohexane, *trans*-1,4-dichlorocyclohexane, and *trans*-1,4-dibromocyclohexane in carbon disulfide.

Infrared spectra have been recorded using the diamond anvil cell,[1] at a temperature approximately 50°.

In determining pressures of liquid samples in the diamond cell, we have found it convenient to use infrared results reported by Drickamer and coworkers.[4] They found that O-H stretching frequencies of alcohols and carbonyl overtone frequencies of ketones dissolved in organic solvents are considerably red-shifted with increased pressure. Thus, an internal standard (such as methanol or cyclohexanone) can be added in small concentrations along with compounds to be studied in CS_2 or other organic solvents. From measurement of the O-H or C=O (overtone) frequencies of the standard (in the 3600- and 3400-cm^{-1} regions, respectively) pressures in the 0-12 kbar range can be determined directly. In a number of the cyclohexane systems, the CH_2 deformation modes (at about 870 cm^{-1}) are also fairly pressure sensitive, and changes in these frequencies can be correlated with those in the compounds studied by Drickamer et al.

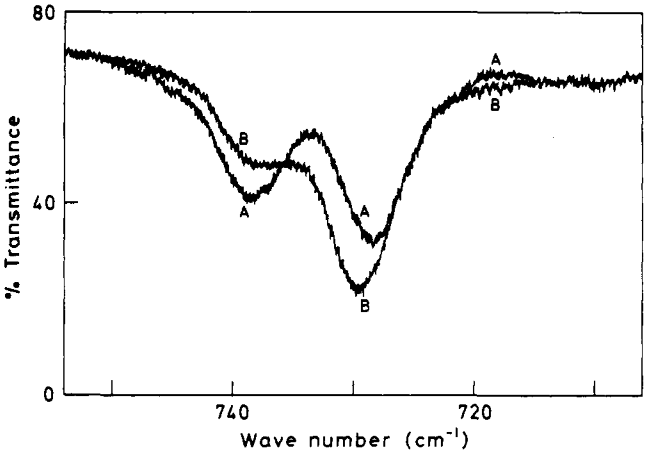

Figure 1. Infrared active C-Br stretching modes of the diequatorial (738) and diaxial (728 cm^{-1}) conformers of *trans*-1,4-dibromocyclohexane (CS_2 solution, 0.12 *M*); pressure, curve (A) 0.4 and curve (B) 6.7 kbar. Corresponding bands in chlorocyclohexane at 732 (e) and 685 cm^{-1} (a) and *trans*-1,4-dichlorocyclohexane at 783 (ee) and 758 cm^{-1} (aa) were employed for the calculations.

Table I. Changes in Conformational Populations with Pressure, and Differences in Partial Molar Volumes

Solute	% increase in *K* per kbar[a, b]	$\Delta\bar{V}$ (cm^3/mol)[b, c]
Chlorocyclohexane	7.3 ± 0.4	−1.87 ± 0.14
trans-1,4-Dichlorocyclohexane	11.5 ± 0.6	−2.8 ± 0.2
trans-1,4-Dibromocyclohexane	15.4 ± 0.6	−3.8 ± 0.2

[a] *K* = [axial]/[equatorial]. [b] Calculated for each compound from least-squares parameters obtained by fitting data to the linear integrated form of eq 1. Approximately 20 intensity ratio measurements were made for each system in the pressure range from 0 to 10 kbar. Uncertainties in reported values are least-squares estimates of standard deviations. [c] Volume changes for conversion of equatorial to axial forms.

By studying pressure effects on the spectra of dilute solutions of several mono- and dihalocyclohexanes in CS_2, we have observed that the conformational equilibria shift markedly in the direction of increased populations of the axially substituted conformers. The bands which are assigned to the e (or ee) species diminish considerably in intensity, whereas the a (or aa) bands increase. For quantitative purposes we have measured integrated intensities of the infrared active C-X stretching bands (X = Cl or Br) in CS_2 solutions containing a few mole per cent of the individual cyclohexane derivatives; pressures have been varied from 0 to about 10 kbar. Figure 1 shows infrared curves for a dilute solution of *trans*-1,4-dibromocyclohexane in CS_2 in the 710-750-cm^{-1} region. We assume that the respective band areas are proportional to concentrations of the conformers; thus the conformational equilibrium constant (*K* = [axial]/[equatorial]) is taken to be directly proportional to the ratio of the axial to the equatorial band areas. Values of the change in conformer partial molar volume (equatorial to axial) are inferred from the relation

$$\Delta\bar{V} = -RT \,\mathrm{d}\ln K/\mathrm{d}P \qquad (1)$$

Table I summarizes least-squares values of changes in conformational population and partial molar volume for the three halocyclohexanes.

Volume changes reported here (−1.87 to −3.8 cm^3/mol), for conversion of equatorial into axial forms, are similar in magnitude to those estimated from proton NMR and ultrasonic relaxation data for the trans to gauche conversion of 1,1,2-trichloroethane.[5] They are much larger than the 0.4% volume decrease estimated for methylcyclohexane (equatorial to axial) from density data.[6] Because lack of information about $\Delta\bar{V}$ for conformational changes has thrown doubt on the value of the acoustic method as a means for determining conformational energy changes,[5] results like those presented here should also be useful in interpreting ultrasonic absorption data.

The observed decreases in volume for conversion of the halogenated cyclohexanes from equatorial to axial forms probably reflect the relatively greater crowding of atoms in a as opposed to e conformers. Thus, the axial conformers have 1-3 (parallel) interactions between a bulky halogen atom and two hydrogen atoms, not present in the equatorial forms. It will be difficult to predict partial molar volumes of particular conformers from knowledge of their structures and van der Waals parameters, partly because of the complicating effects of packing solvent molecules around the individual solutes, but it may be possible to determine empirically the magnitudes of volume effects which are due to atomic contacts of particular types. Whether or not such effects are additive and transferable from compound to compound can only be determined when additional volume data of the type presented here become available.

Acknowledgment. Financial support from The Norwegian Research Council for Science and The Humanities is gratefully appreciated.

References and Notes

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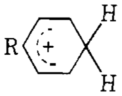
The Baker-Nathan Effect on Solvation Energies of Benzenonium and Other Organic Ions

Sir:

Hehre, McIver, Pople, and Schleyer[1] have recently presented conclusive evidence that in the gas phase alkyl groups follow the inductive order (Me < Et < *i*-Pr < *t*-Bu) in their ability to stabilize arenonium ions ($C_6H_6R^+$). A


= ($C_6H_6R^+$)

contrary ordering of relative stabilities has often been reported in solution and is called the Baker-Nathan effect. Thanks to the work of Hehre et al.[1] the origin of the inverted ordering can now be attributed unequivocally to solvation factors as was proposed originally by Schubert and Sweeney.[2] Combination of the gas phase data with heats of vaporization and heats of ionization of the alkyl benzenes in superacid solution allows calculation of the solvation enthalpies of the benzenonium ions.

Table I. Relative Enthalpies for Ionization and for Solution of Arenes and Arenonium Ions (in kcal mol^{-1})

Arene	$\delta\Delta H_i{}^a$ (gas)	$\delta\Delta H_i{}^b$ (ma)	$\delta\Delta H_S{}^c$ (C_6H_5R) (g → MeOH)	$\delta\Delta H_S$ ($C_6H_6R^+$)
C_6H_5Me	0.0	0.00	0.00	0.00
C_6H_5Et	−0.85 ± 0.1	2.84	−1.19	2.50 ± 0.75
C_6H_5-*n*-Pr	−1.7 ± 0.1	2.13	−1.87	1.96 ± 0.39
C_6H_5-*i*-Pr	−2.1 ± 0.1	2.61	−1.85	2.86 ± 0.58
C_6H_5-*t*-Bu	−2.3 ± 0.5	3.87	−2.57	3.60 ± 0.96

[a] From ref 1. Relative enthalpies of ionization in the gas phase (ΔH_i (gas)) are equated to observed standard free energies for $C_6H_5R + C_6H_6Me^+ \rightleftharpoons C_6H_6Me^+ + C_6H_5R$, in the opposite sense to the process reported in ref 1. [b] These values correspond to the relative heats for transfer from methanol at −60° to ma (11.5% SbF_5 in HSO_3F) at −60°. They differ slightly from those used in ref 1 which were based on earlier work from this laboratory using CCl_4 at 25° as a reference state. [c] The assumption that $\Delta G^\circ{}_i$ (gas) = $\Delta H^\circ{}_i$ (gas) is based on the reasonable assumption that $\Delta S^\circ{}_i$ (g) = 0 for an isodesmic proton exchange reaction in the gas phase for a series of structurally similar compounds. It has some support from experiment (Kebarle) and carries the important implication that $\Delta H^\circ{}_i$ (gas and $\Delta G^\circ{}_i$ (gas) are temperature invariant since $(\partial G^\circ/\partial T) = \Delta S^\circ{}_i = 0$. [d] Values in this column were calculated through the type of cycle previously employed by us (E. M. Arnett, *Acc. Chem. Res.*, **6**, 404 (1973)); thus $\delta\Delta H_S(C_6H_6R^+) = \delta\Delta H_i(\text{ma}) - \delta\Delta H_i(\text{gas}) + \delta\Delta H_S(C_6H_5R)$.

In Table I are presented the heats of ionization in the gas phase ($\delta\Delta H_i$(gas)), heats of ionization in 11.5% SbF_5-HSO_3F (magic acid) (ma) at −60° ($\delta\Delta H_i$ (ma)) the heats of solution at −60° ($\delta\Delta H_s$ (C_6H_5R) of the arene from the gas phase to methanol (the reference solvent), and finally the heats of solvation of the benzenonium ions ($\delta\Delta H_s$ $C_6H_6R^+$) from the gas phase into ma at −60°. All values are taken relative to toluene as reference compound and are derived from data in ref 1 or Table II.

In previous studies[3,4] heats of benzenonium ion formation were estimated using heats of transfer from CCl_4 at 25° to ma at −65°. The values presented here are based instead on methanol at −60° as the reference state. Although the choice of inert solvent should have a minor effect on the derived ionization or solvation energies, we believe that methanol is preferable since it is a liquid at −60° (CCl_4 freezes at −23°). Also methanol is probably a better medium as a model for the behavior to be expected of HSO_3F-SbF_5 if it could be divested of its protonating ability. Larsen, Bouis, and Glass[5] have shown that small Baker-Nathan orders for arenes can be generated merely through heats of transfer from solvents of low to high cohesive energy density (CED). We wish to minimize any such artifacts in the data presented here. In this sense, we believe that methanol should be a better model for HSO_3F than is CCl_4.

The heat of solution of a pure liquid solute in any solvent is actually the heat of transfer of the solute dissolved in itself to high dilution in the solvent in question. Since the CED's of the arenes decrease from 79.2 for toluene to 69.7 for *tert*-butyl benzene, it is reasonable to expect that heats of solution could change from a false "inductive order" in solvents of low CED to a false "Baker-Nathan order" in solvents of high CED since in the absence of internal energy changes

$$\Delta H_{\text{transfer}} \simeq [\text{CED}_{\text{solvent}} - (\text{CED})_{\text{ArR}}]_{\text{sol}} V_{\text{ArR}}$$

where V_{ArR} is the molar volume of the arene solute.

In contrast, transfer of a neutral, nonpolar solute from the gas phase to an inert solvent will result in an exothermic interaction which will increase in a regular progression as a