Table IV. Calculation of $(NO)_2$ Cis-Trans Energy Difference with Expanded Basis Sets

Basis	$-E$(cis), au	$-E$(trans), au	ΔE, kcal/mol
$(9,5) \rightarrow \langle 4,2\rangle$	258.250 09	258.254 73	−2.91
$(9,5,1) \rightarrow \langle 4,2,1\rangle$	258.432 29	258.432 41	0
$(10,6,1) \rightarrow \langle 5,3,1\rangle$	258.475 71	258.478 39	−1.68

With the (7,3) basis set, the cis rotational barrier is calculated to be 5.0 kcal and the trans barrier 3.6 kcal. The experimental estimates of the barriers in N_2O_3 and N_2O_4 are 1[31] and 2–3[32] kcal, so the ab initio barriers are quite probably too high, as was also the ab initio N_2O_4 barrier.[23]

Conclusion

The nitric oxide dimer has been shown to have two preferred conformations: planar cis and planar trans. The wave functions, structures, and force fields show the importance of lone pair delocalization in weakening the N–N bond and a weak O···O bond in stabilizing the cis form. The calculations form a basis for possible experimental observation of the low-lying vibrations involving the interesting N–N bond and of a direct determination of the structures by microwave spectroscopy (cis dipole moment of 0.6 D) or electron diffraction.

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Vapor Phase Hydrogen Bonding of 2,2,2-Trifluoroethanol with Acetone

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Abstract: Thermodynamic data for the 1:1 hydrogen bonded complex of trifluoroethanol with acetone have been obtained from vapor density measurements at 25, 35, and 45 °C. The equilibrium constant for formation of the 1:1 vapor complex at 25 °C is 47.3 M⁻¹. $\Delta E°$ for complex formation is −6.79 kcal/mol. A comparison of these thermodynamic data with previously reported data for the 1:1 complex in CCl_4 solution shows that the complex is significantly more stable in the vapor phase than in CCl_4 solution. With the aid of literature data the complete thermodynamic cycle for transfer of monomers and the 1:1 complex between vapor and CCl_4 has been constructed to illustrate solvation effects on the trifluoroethanol–acetone complex.

There have been literally hundreds of published reports of molecular orbital calculations of the energy of formation of hydrogen bonded complexes. Yet, there are almost no experimental vapor data with which to compare the theoretical results. In the entire chemical literature there are no more than ten publications which claim to give reliable thermodynamic data for 1:1 hydrogen bonded complexes in the vapor phase. Good thermodynamic data for vapor phase complexes are important not only because they offer experimental energies which can be directly compared with the theoretical calculations but also because they give a firm foundation on which to base considerations of solvent effects on hydrogen bond formation.[1]

Previous reports from this and other laboratories have shown

that thermodynamic constants for hydrogen bonding and charge-transfer reactions are generally dependent upon the medium in which reaction occurs.[2] In particular, no solvent has been found which is truly inert in comparison with the gas phase as a reference medium. For example, thermodynamic data for hydrogen-bonded complexes which have been studied in both vapor and condensed phases indicate that carboxylic acid dimers[3,4] and methanol–amine complexes[1,5] are less stable in relatively inert solvents than in the vapor phase.[6] Moreover, in the case of most hydrogen-bonded complexes, stabilities decrease as the solvent is varied from aliphatic hydrocarbon, to chlorinated or aromatic hydrocarbon, to polar liquid.

Many workers continue to hope, however, that solvent effects on complex formation equilibria will nearly cancel as the

Table II. Vapor Phase Association Constants for TFE–Acetone

T, °C	K_{11}, Torr^{-1}	K_{11}, M^{-1}	No. of data points	RMSD,[a] Torr
25	$(2.55 \pm 0.02) \times 10^{-3}$	47.3	38	0.053
35	$(1.72 \pm 0.01) \times 10^{-3}$	33.0	99	0.090
45	$(1.160 \pm 0.005) \times 10^{-3}$	23.0	48	0.031

[a] Root mean square deviation in $\pi_{acetone}$.

Table III. Thermodynamic Constants for the TFE–Acetone Complex

Vapor	CCl$_4$	E and C prediction
25 °C	24 ± 1 °C	
K(M^{-1}) = 47.3	K(M^{-1}) = 7.3	
$\Delta E° = -(6.79 \pm 0.13)$ kcal/mol	$\Delta E° = \Delta H° = -(5.05 \pm 0.2)$ kcal/mol	$\Delta H° = -4.88$ kcal/mol

medium is changed from vapor to solvent or from one solvent to another. Thus it is frequently assumed that activity coefficient effects will be negligible throughout wide ranges of concentration in donor–solvent systems, although physical theories of solution indicate that large activity coefficient changes are to be expected, even in the absence of "specific" interaction with a solvent. A commonly used scheme for predicting adduct formation enthalpies (the E and C correlation) involves the assumption that heats of formation of complexes in solvents such as CCl$_4$ or hexane will be essentially the same as in vapor.[7]

Calculations based on classical and statistical thermodynamic theories have been of some use in predicting the effects of nonpolar solvents on complex formation energies and free energies.[2,8] However, a recent analysis of solvent effects on partition functions of hydrogen-bonded adducts and their constituent molecules predicts that hydrogen bond stabilities should be enhanced in the liquid state, primarily because of a translational free volume effect.[9] In fact, this prediction runs counter to experimental evidence that hydrogen-bonded complexes are in general less stable in condensed phases than in the vapor state.

Clearly, theoretical explanations of solvent effects must remain speculative until more experimental information about adduct stabilities in various media becomes available. There are relatively few systems which can be conveniently studied in both condensed and vapor phases. 2,2,2-Trifluoroethanol (TFE) is sufficiently volatile to permit accurate measurement of thermodynamic properties of its vapor phase complexes, and there are for comparison literature data for several TFE–base adducts in CCl$_4$.[10,11] The present report gives thermodynamic data for the 1:1 complex of TFE with acetone in the vapor phase.

Experimental Section

2,2,2-Trifluoroethanol from Aldrich, Gold Label grade, was used after passing the vapor through a 4-A molecular sieve column previously heated and evacuated to a pressure of $\sim 10^{-4}$ Torr. Reagent grade acetone (J. T. Baker Co.) was distilled from P$_2$O$_5$ through a 20-plate column and kept in vapor contact with anhydrous CaSO$_4$. The vapor density apparatus and technique were similar to those used previously.[12] Thermostat bath temperatures were controlled to ±0.01 °C. Pressures were measured with a Texas Instruments pressure gauge with minimum resolution of 0.003 Torr, absolute. The experimental technique consisted of volumetrically adding increments of acetone to (1) the evacuated system to establish a calibration curve of volume added vs. pressure and (2) to the apparatus filled with an initial fixed pressure of TFE (20 to 70 Torr).[13] Table I (supplementary material) presents the experimental TFE–acetone vapor density data.

Results and Discussion

The nonideality of acetone vapor in the range from 0 to 70 Torr was accounted for by using dimerization constants derived from the work of Lambert et al.[14] The formal or ideal gas pressure of acetone in the mixed system is obtained by combined use of the calibration curve for acetone addition and the derived K_2 value. Equation 1 gives the expression for the formal acetone pressure in the mixed system.

$$\pi_{acetone} = p_B + 2K_2 p_B{}^2 + K_{11} p_A p_B \tag{1}$$

p_B and p_A are monomer pressures of acetone and TFE, respectively, and K_{11} is the TFE–acetone association constant. The K_2 correction is quite small; for example, the difference between observed pressure and formal pressure of acetone vapor (with no TFE present) at the maximum acetone pressure used is ca. 0.5%. TFE vapor was assumed to be an ideal gas over the present temperature and pressure range. The error involved in this approximation can be estimated from a previous PVT study of TFE vapor in this laboratory[15] to contribute no more than 0.3% in the final TFE–acetone 1:1 association constant. The TFE pressure in the mixed system is then the measured initial TFE pressure (no acetone present) and is expressed by eq 2.

$$\pi_{TFE} = p_{TFE} = p_A + K_{11} p_A p_B \tag{2}$$
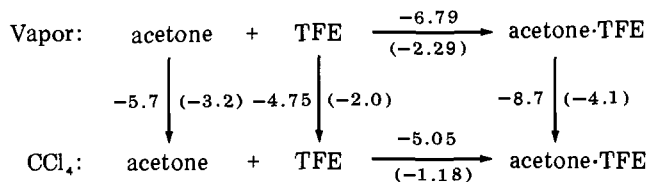
The measured total pressure for the mixed system is given by

$$P_{total} = p_A + p_B + K_{11} p_A p_B + K_2 p_B{}^2 \tag{3}$$

Since $\pi_{acetone}$ is the observable in greatest error we seek to determine a K_{11} value which minimizes the deviations between π_{obsd} and π_{calc}. Equations 2 and 3 are solved for p_A and p_B values using an initial K_{11}; these values are then used to calculate $\pi_{acetone}$ via eq 1. Values of K_{11} which minimize the root-mean-square deviation at the various temperatures are listed in Table II.[16]

A standard state on the molarity basis should be used for comparing thermodynamic data for association reactions occurring in both vapor and solution phases. The least-squares values of $\Delta E°$ and $\Delta S°$ for the vapor phase association of TFE and acetone are $-(6.79 \pm 0.13)$ kcal/mol and $-(17.1 \pm 0.4)$ cal/(deg mol), respectively. Table III compares the results of this work with data for the 1:1 TFE–acetone complex in CCl$_4$[11] and the ΔH value predicted by the E and C equation, using parameters from ref 7.

The change in formation energy of the TFE–acetone complex, on transfer from the vapor phase into CCl$_4$, is comparable to that observed for transfer of the methanol–diethylamine complex from vapor into n-hexadecane.[1] With the aid of literature data,[11,17-20] we may construct the following thermodynamic cycle for the TFE–acetone complex, including energy and free energy values for both the transfer reactions and the complex formation reaction.

Vapor: acetone + TFE $\xrightarrow[(-2.29)]{-6.79}$ acetone·TFE

-5.7 (−3.2) −4.75 (−2.0) -8.7 (−4.1)

CCl$_4$: acetone + TFE $\xrightarrow[(-1.18)]{-5.05}$ acetone·TFE

Numbers in parentheses are $\Delta G°$ (kcal/mol) values based on the unit molarity ideal dilute solution standard state. The remaining quantities are energies ($\Delta E°$) for the various steps in the cycle. The transfer energies and free energies for the 1:1

complex are derived, by difference, from the other steps in the cycle. There may be significant errors in the transfer free energies for monomers and complex (on the order of 0.2 to 0.3 kcal/mol) but these values are sufficiently accurate for the purpose of comparing gas phase and condensed phase thermodynamic constants for the complex.

It is apparent from the above cycle that the transfer energies and free energies of the individual components are not small compared with ΔE° and ΔG° for the association reaction. The energy of transfer of the complex into CCl_4 is 83% that of the separated monomers; the corresponding free energy of transfer is 79% that of the monomers. Thus the TFE–acetone system is typical of several previously studied hydrogen-bonded systems, for which the transfer energy and free energy fractions (α and α') are significantly less than unity.[2] The present results clearly indicate that the transfer energy and free energy of the complex are not even approximately cancelled by the transfer energies and free energies of the constituent molecules.

The fact that adduct enthalpies are not the same in so-called "inert" solvents as in the gas phase limits the utility of correlations of condensed phase ΔH° values with factors attributable to the individual interacting solutes. Since each formation enthalpy involves a contribution from the solvent, it will not be possible to analyze condensed phase data to obtain empirical constants (e.g., the E and C parameters) which are characteristic only of the *isolated* donor and acceptor molecules. We agree with Tamres that the E and C equation might be useful for predicting vapor phase enthalpies if new E and C parameters based on vapor phase data were obtained.[21]

Data of the type presented here are needed to test the reliability of theories of solution in predicting transfer energies and free energies of complexing systems. Measurements of energies and free energies of complex formation reactions in vapor and condensed phases are intrinsically valuable in showing the existence of solvent effects. However, such results can be made even more useful when sufficient thermodynamic data are obtained for the monomers so that the complete thermodynamic solvation cycle can be presented. Information like this is available for very few complexing systems.

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