that the maximum rate occurs at a much smaller $-\Delta G$ than in MTHF and that the rate falloff at large exothermicity is much more pronounced. In less polar isooctane mildly exothermic reactions are speeded up by factors as large as 10^3 while strongly exothermic ones are slowed down by factors as large as $10^{1.8}$. The possible formation of excited states adds a complicating factor to this relationship and probably accounts for the exceptionally high rates observed for naphthoquinonyl and dichlorobenzoquinonyl in isooctane.[23]

We believe that our observation of diminishing rates with very negative ΔG is the first unambiguous demonstration of the existence of the so-called inverted region in solution ET reactions. The failure of previous efforts can probably be attributed to the fact that most of the ET reactions studied were intermolecular, where diffusion sets a limit to the observable rate, thus cutting off the top of the curve shown in the figure. In support of this conclusion is the observation that the bimolecular rate constants measured with models of type A–Sp and B–Sp vary only by a factor of 4.

The ΔG and solvent dependence of the ET reactions reported here are very different from predictions made by classical physical–organic reasoning and serve to confirm conclusions drawn by one of us from intermolecular ET reactions in rigid glasses.[3-5] In addition, the work emphasizes the fact that ET across an insulating barrier as wide as 10 Å can occur astonishingly fast (~100 ps) if conditions are maximized.

Besides dependence of ET rates on exthermicity and solvent polarity, other important questions concern temperature, distance, and geometry dependences. Such experiments are in progress at the present time.

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S_N2 Reaction Profiles in the Gas Phase and Aqueous Solution

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Striking demonstraton of the importance of medium effects is provided by bimolecular nucleophilic substitution reactions involving anions and polar molecules. The rates in the gas phase and solution vary over 20 orders of magnitude. Explanations have focused on preferential stabilization of the reactants relative to the charge-dispersed transition state by polar, especially protic, solvents.[1-3] However, the detailed form of the reaction surfaces in solution is unknown. The traditional assumption of a unimodal profile needs critical examination, particularly since the gas-phase reaction is characterized by a double-well surface, with unsymmetrical ion–dipole complexes as minima and a symmetrical transition state.[3,4] Conceivably, analogues of the gas-phase minima and new solvent-separated ones may be present in solution. In this communication, we report the first computation of an energy profile for an S_N2 reaction ($Cl^- + CH_3Cl'$) in aqueous solution. The present statistical mechanics simulations go significantly beyond previous quantum mechanical investigations of S_N2 reactions in the gas phase[5,6] or in the presence of a few water molecules.[7] The latter calculations have bearing on studies of gas-phase clusters[8] but do not include the important effect of bulk solvent reorganization, which contributes significantly to the barrier in solution. The present simulations explicity include a large number of water molecules as well as thermal averaging.

The calculation involved three steps: (i) determination of the gas-phase reaction surface, (ii) development of potential functions to describe the solute–solvent interactions, and (iii) Monte Carlo simulations of the reaction in solution. Ab initio 6-31G* calculations were used to construct the gas-phase energy profile.[9] For fixed values of r_{CCl}, the remaining geometric parameters were optimized in C_{3v} symmetry. The reaction coordinate was defined as $r_c = r_{CCl'} - r_{CCl}$, which is symmetric about the transition state, ($r_c = 0$). The calculated geometric parameters and total energies were fit to analytical functions of r_c. The resultant energy profile (Figure 1, dashed curve) contains two minima flanking the symmetric transition state. The calculated energy of the ion–dipole complex, **1**, relative to the reactants (-10.3 kcal/mol) as well as the energy of the transition state, **2**, relative to **1** (13.9 kcal/mol) are in accord with the experimental complexation enthalpy (8.6 kcal/mol)[10] and intrinsic barrier (~10.2, 11.6 ± 1.8 kcal/mol).[3b,11]

Intermolecular interactions were described with potential functions in the 12–6–1 form and were assumed to be pairwise additive. The parameters for the water molecules correspond to the TIP4P model.[12] A novel and clearly necessary point is that the charges and Lennard–Jones terms for the atoms in the solute cluster vary along the reaction coordinate. These parameters and their dependence on r_c were determined from 6-31G* calculations on a large number of geometries of $CH_3Cl_2^- + H_2O$ spanning the reaction coordinate. The details are provided as supplementary material.

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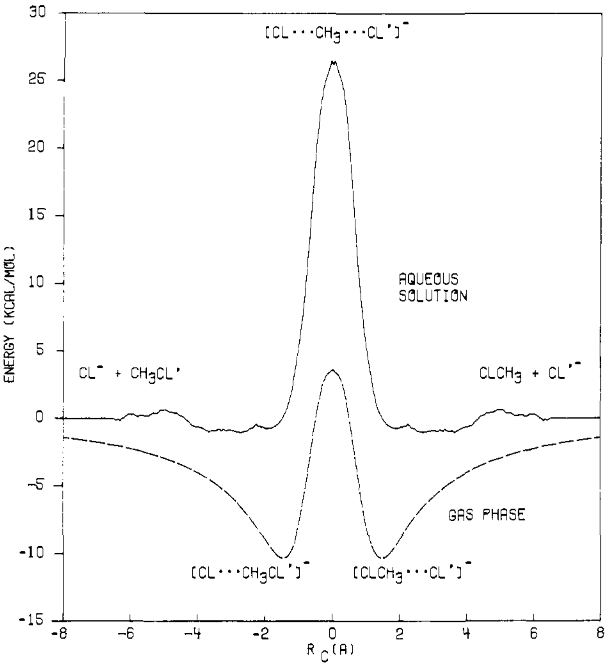

Figure 1. Calculated internal energies in the gas phase (dashed curve) and the potential of mean force in aqueous solution (solid curve) for the system $[\mathrm{ClCH_3Cl}]^-$ as a function of the reaction coordinate, r_c (in angstroms).

The principal goal of the solution simulations was to obtain the potential of mean force, $w(r_c)$, which represents the relative free energy of the system as a function of r_c. The function is given by $-kT \ln g(r_c)$, where $g(r_c)$ is the probability of occurrence of each value of r_c. Precise computation of $g(r_c)$ requires the use of importance sampling methods.[13] Thus, simulations were carried out for six overlapping regions covering the entire reaction. The solute was constrained within limited ranges of r_c by imposing a harmonic force. Furthermore, an additional biasing function, $\exp(-25r_c^2)$, was included to enable sufficient sampling near the high-energy transition state. All calculated properties were normalized to remove the effects of this non-Boltzmann sampling.[13] The $g(r_c)$ from the different "windows" were spliced together at points of maximum overlap to form a single distribution from which $w(r_c)$ was obtained.

Monte Carlo simulations were executed for the solute cluster and 250 water molecules in the NPT ensemble at 25 °C and 1 atm. As in previous work, periodic boundary conditions and a preferential sampling algorithm to enhance solute-solvent statistics were employed.[14] Equilibration for 1000-2000K configurations was followed by averaging over 2600K configurations for each window. In all, this required ca. 50 h on a Cyber 205 computer.

The calculated potential of mean force (Figure 1, solid curve) is distinctly different from the gas-phase profile. Part of the difference is because the former is a free energy curve while the latter indicates the change in internal energy (for the hypothetical vibrationless system at 0 K). The minima in the gas phase would be less deep on the free energy scale because of the large negative entropy accompanying their formation from the separated species.[15] However, the entropy change from **1** to **2** is expected to be much smaller leaving the intrinsic barrier essentially unchanged.[16] Clearly, solvation leads to a flattening of the ion-dipole minima and to a large increase in the free energy of activation. Although putative minima exist, they are very shallow and would have negiligible influence on the reaction kinetics. Thus, the calculations firmly support the conventional view of a unimodal energy surface in aqueous solution. The calculated free energy of activation (26.3 ± 0.5 kcal/mol)[17] is in quantitative agreement with the experimental value (26.6 kcal/mol).[18] This along with the reasonable computed heat of solution for the reactants (88 ± 6 kcal/mol)[19] supports the viability of the computational model, though consideration of vibrational effects and the full multidimensional nature of the surface are desirable.

The sharp onset of the barrier at the position of the ion-dipole complex in solution is also interesting. It reveals that the desolvation of the ion up to this stage is compensated by the ion-dipole attraction. The enhanced barrier in solution then results primarily from less solute-solvent attraction for the charge delocalized transition state than for the separated reactants. Further structural and thermodynamic analyses of this system will be reported shortly.[20]

Registry No. $\mathrm{CH_3Cl}$, 74-87-3; $\mathrm{Cl^-}$, 16887-00-6.

Supplementary Material Available: Details of the intermolecular potential functions used in the simulations (4 pages). Ordering information is given on any current masthead page.

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[15] At 298 K, ΔH for the formation of the ion-dipole complex is -8.6 kcal/mol, while ΔG for the process is only -4.1 kcal/mol.[10]

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Reactions of Coordinated Molecules. 40. Addition of a Pt-H Bond across Metal Acetylide C-C Triple Bonds: A Direct Route to Dinuclear μ-Vinylidene Complexes

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Recent theoretical calculations have supported the general opinion that the orbitals of the carbon-carbon triple bonds of metal acetylide ligands do not interact greatly with the valence orbitals of the metal atoms to which they are bonded.[2] Because M-H bonds are known to add to the carbon-carbon triple bonds of alkynes, a similar addition to metal acetylides might provide an interesting and general route to the preparation of homo- and heterodinuclear complexes. The first example of this type of reaction is reported below.

When the platinum phenylacetylide complex, *trans*-$\mathrm{Pt(PEt_3)_2(C{\equiv}CPh)_2}$[3] (**1**), is treated with 1 equiv of [*trans*-$\mathrm{Pt(PEt_3)_2(H)(acetone)]BF_4}$[4] (**2**), in acetone solution at 25 °C for 20 min,

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