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Theoretical Study on Carbocation Formation Reactions. Resonance Demands and Transition Structures

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Ab initio molecular-orbital calculations were carried out for two carbocation-generating reactions, the S_N1 reaction of protonated 1-phenylethyl alcohol (H_2O leaving group) and the acid-catalyzed hydration of styrene. Separated reactants, reactant complexes, transition states (TSs), product complex, and separated products were optimized at MP2/6-31G* and the vibrational frequencies were analyzed. The S_N1 TS lies halfway between the reactant and the product with respect to the bond lengths, charge distribution, and secondary deuterium isotope effects. The degree of the π-orbital overlap between the benzylic carbon and the phenyl ring is almost the same in the S_N1 TS and the 1-phenylethyl cation. The proton-transfer TS of the hydration, on the other hand, reaches earlier, and the π-orbital overlap in the TS is less effective. These differences are responsible for the difference in the experimental substituent effect reported in the literature for the two reactions.

Linear-free energy relationships have been widely used in exploring of mechanistic hypotheses in a variety of reactions.[1)] In particular, the Yukawa–Tsuno equation (an extended Hammett equation, 1)[2)] has been successfully applied to benzylic solvolyses, in which a positive charge is generated at the conjugative position with the aryl group.[3)]

$$\log(k/k_\circ) = \rho(\sigma^\circ + r^+\Delta\overline{\sigma}_R^+) \qquad (1)$$

In this equation, σ° is a normal substituent constant, $\Delta\overline{\sigma}_R^+$ is a resonance substituent constant ($\Delta\overline{\sigma}_R^+ = \sigma^+ - \sigma^\circ$), and r^+ is resonance demand parameter reflecting the degree of the π-interaction between a para π-donor substituent and a positively charged reaction center. The r^+ value is known to increase significantly as the positive charge on the benzylic carbon is destabilized by substituents on the carbon, giving a continuous spectrum from $r^+ = 1.00$ for α-cumyl (1-methyl-1-phenylethyl) chlorides, via $r^+ = 1.29$ for benzyl tosylates to $r^+ \geq 1.5$ for extremely electron-deficient carbocation systems, such as 2,2,2-trifluoro-1-phenylethyl tosylates.[3)]

The acid-catalyzed hydration of styrene and the S_N1 solvolysis of the corresponding substrate generate the same benzylic carbocation intermediate. However, the r^+ values for the hydration of substituted styrenes are known to be smaller than those for the solvolysis,[4—6)] e.g., $r^+ = 0.70$ and 1.15 for acid-catalyzed hydration of α-methylstyrene and α-trifluoromethylstyrene while 1.00 and 1.39 for the solvolysis of α-cumyl chloride and 1-phenyl-1-(trifluoromethyl)ethyl tosylate, respectively.[6c)] The difference in the r^+ value should primarily arise from the difference in the transition structures leading to the carbocation, because the protonation on the methylene carbon to give a carbocation is the rate-determining step of the hydration according to the currently accepted mechanism (Eq. 3).[7)]

In order to interpret the r^+ value in terms of the transition structures, a comparison of the resonance demand for the TS and the cation intermediate would be essential. From this point of view, we have recently investigated the substituent effects on the thermodynamic stabilities of benzylic cations ($ArCR^1R^{2+}$) in the gas phase.[6)] Several important points emerged from the data summarized in Table 1: (1) the ρ values are considerably large in the gas-phase equilibria compared to the solution kinetics, while the r^+ values are in similar magnitudes for both systems; (2) the r^+ value for the gas-phase equilibria decreases with the electron-donating ability of substituent R^1, and R^2 increases, whereas the ρ value stays essentially constant; (3) the magnitudes of r^+

Table 1. Summary of Substituent Effects for the Thermodynamic Stabilities of Carbocations in the Gas Phase, Acid-Catalyzed Hydration of Styrenes, and the S_N1 Solvolysis of the Corresponding Precursors

$ArC^+(R^1)R^2$		Cation-stability[a)]		Solvolysis[b)]		Hydration[c)]	
R^1	R^2	$-\rho_{gas}$	r^+_{gas}	$-\rho_{sol}$	r^+_{sol}	$-\rho_{hyd}$	r^+_{hyd}
CH_3	CH_3	9.5	1.00	4.59	1.00	2.99[d)]	0.70[d)]
H	CH_3	10.1	1.14	4.97	1.15	3.56[e)]	0.94[e)]
H	H	10.3	1.29	5.23	1.29	—	—
CH_3	CF_3	10.0	1.41	6.29	1.39	4.77[f)]	1.15[f)]
H	CF_3	10.6	1.53	6.05	1.53	—	—

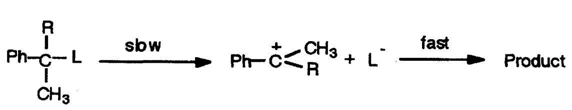
a) Ref. 6. b) Ref. 3. c) Recalculated using data in Ref. 8 to Ref. 10. d) Ref. 8. e) Ref. 9. f) Ref. 10.

Table 2. Selected Geometrical Parameters, Group Charge Density, and Potential Energies Calculated at MP2/6-31G*[a)]

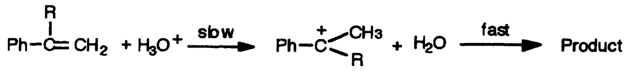
	1-Phenylethyl alcohol, protonated	TS1	Cation–H_2O complex	1-Phenylethyl cation	TS2	Styrene–H_3O^+ complex	Styrene
C_1C_7	1.474	1.420	1.395	1.390	1.457	1.478	1.472
C_7C_8	1.500	1.481	1.469	1.470	1.367	1.353	1.343
C_7O	1.641	2.077	2.639				
C_8C_{10}	1.093	1.091	1.098	1.100	1.608	2.118	
$C_8C_7C_1C_6$	−37.2°	−13.6°	0.5°	0.0°	20.6°	36.0°	27.2°
$H_9C_7C_1C_2$	−8.3°	8.2°	2.3°	0.0°	14.9°	38.3°	25.3°
Charge on Ph	0.225	0.369	0.468	0.548	0.196	0.111	−0.002
Relative energy	−1.7	0.9	0.0	11.7[b)]	17.6	15.7	46.4[b)]

a) Bond lengths are in Å and dihedral angles are in degree. Energy is in kcal mol^{-1} relative to 1-phenylethyl cation–H_2O complex.
b) Energy of the cation + H_2O. c) Energy of styrene + H_3O^+.

in the gas-phase equilibria are in complete agreement with those in the S_N1 solvolyses of the corresponding precursors, whereas the r^+ values are significantly smaller in the hydration kinetics.



(2)



(3)

Loudon and Berke[5)] previously discussed the different behaviors in the substituent effect between hydration and solvolysis on the basis of extended Hückel MO calculations using model transition structures of the reactions of α-methylstyrene and α-cumyl chloride to give the α-cumyl cation. We now report on the results of ab initio MO calculations for the rate-determining steps of reactions 2 and 3, in which R = H and L in Eq. 2 is H_2O^+. The purpose of this study is two-fold: First, it is to clarify the reason for the different r^+ values for the two reactions which give the same cation intermediate, and second it is to analyze the meaning of the similar magnitudes in r^+ for the gas-phase equilibria and the solvolysis kinetics. Since there is no change in the charge between the reactant and the intermediate in both reactions, neglecting solvent effects is expected to cause no serious change in the structure of the TS. In fact, S_N1 solvolyses of substrates which have a charged leaving group have been shown to exhibit little solvent effect.[11)]

Calculation Method

All calculations were carried out at the MP2/6-31G* level[21)] using Gaussian 94.[13)] Reactants, complexes, transition structures, and products were fully optimized and were identified by means of a full analysis of the vibrational modes at those stationary points. Isotope effects were calculated from the scaled vibrational frequencies by using Eq. 4; here, $\nu^{\ddagger}$ represents the reaction-coordinate frequency and u denotes $h\nu/kT$, in which h and k are the Planck constant and the Bolzmann constant, respectively. All results refer to a temperature of 298.15 K.

$$\frac{k_1}{k_2}=\left[\frac{\nu_{L1}^{\neq}}{\nu_{L2}^{\neq}}\right]\frac{\prod\limits^{3n-6}\frac{u_{2i}}{u_{1i}}\prod\limits^{3n-6}\left(\frac{1-e^{-u_{1i}}}{1-e^{-u_{2i}}}\right)\exp\left[\sum\limits^{3n-6}(u_{1i}-u_{2i})/2\right]}{\prod\limits^{3n-7}\frac{u_{2i}^{\neq}}{u_{1i}^{\neq}}\prod\limits^{3n-7}\left(\frac{1-e^{-u_{1i}^{\neq}}}{1-e^{-u_{2i}^{\neq}}}\right)\exp\left[\sum\limits^{3n-7}(u_{1i}^{\neq}-u_{2i}^{\neq})/2\right]}. \quad (4)$$

Results and Discussion

As summarized in Fig. 1, protonated 1-phenylethyl alcohol gives a transition state (**TS1**), which is 2.6 kcal mol^{-1} higher in energy than the reactant. **TS1** leads to a 1-phenylethyl cation–water complex (product complex). The complex is more stable than the separated products (cation + water) by 11.7 kcal mol^{-1}. The barrier height for the S_N1 reaction was calculated to be low, probably due to the high nucleofugality of the H_2O leaving group. In the hydration process, styrene and water first form an initial complex, which then produces a product complex via a transition state (**TS2**). **TS2** lies 1.9 kcal mol^{-1} higher than the initial complex. The selected geometrical parameters and potential energies of

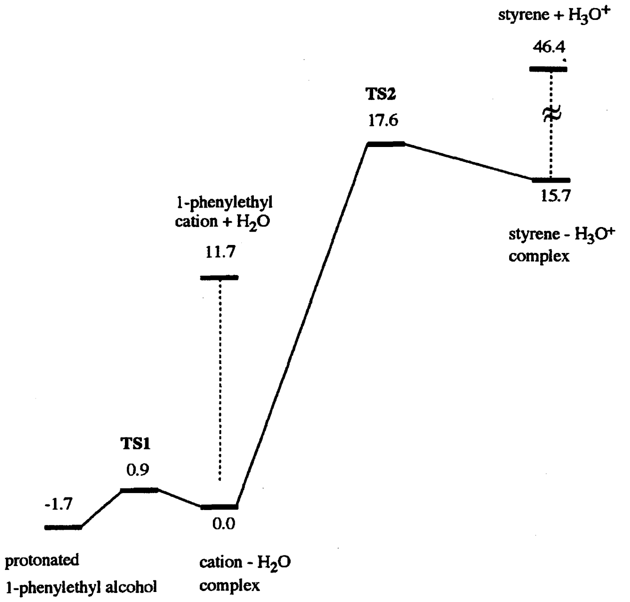


Fig. 1. Reaction profile for the S_N1 solvolysis and the acid-catalyzed hydration at MP2/6-31G*. Energies are in kcal mol^{-1}.

these species at MP2/6-31G* are summarized in Table 2. Calculated kinetic isotope effects and equilibrium isotope effects are listed in Table 3.

S_N1 Reaction. Geometrical Features. Protonated 1-phenylethyl alcohol has a structure such that the leaving group H_2O lies out of the phenyl ring plane (the dihedral angle $OC_7C_1C_2$ is 77.4°, Chart 1). The C_7O bond length is 1.641 Å, which is larger than the normal C–OH bond length (1.43 Å), and the two dihedral angles ($C_8C_7C_1C_6$, and $H_9C_7C_1C_2$) are −37.2° and 8.3°. The distribution of the positive charge into the phenyl ring is small for the species (Table 1).

The geometry of the 1-phenylethyl cation-water complex (product complex) is very similar to that of the 1-phenylethyl cation, although the energy of the product complex is lower than that of the 1-phenylethyl cation + H_2O by 11.7 kcal mol^{-1}. For example, the C_1C_7 bond lengths are 1.395 and 1.390 Å, respectively. In addition, the coplanarity between the phenyl ring and the ethyl moiety is excellent in both cases (vide infra) revealing that the vacant p-orbital of the benzylic carbon atom can completely overlap with the benzene π-orbital in the cation.

Table 3. Calculated Kinetic and Equilibrium Isotope Effects for the S_N1 and the Hydration at MP2/6-31G*[a)]

	S_N1		Hydration[b)]	
	TS1	1-Phenylethyl cation	TS2	1-Phenylethyl cation
α-^{13}C	1.010	0.995	1.009	1.002
α-D_1	1.089	1.219	0.985	0.979
β-^{13}C	1.005	1.007	1.013	0.991
β-D_3 (sec)	1.100	1.205		
β-D_1 (pri)			2.976	0.977
β-D_2 (sec)			0.986	0.911

a) Calculated 25 °C. b) Isotope effects are based on styrene–H_3O^+ complex.

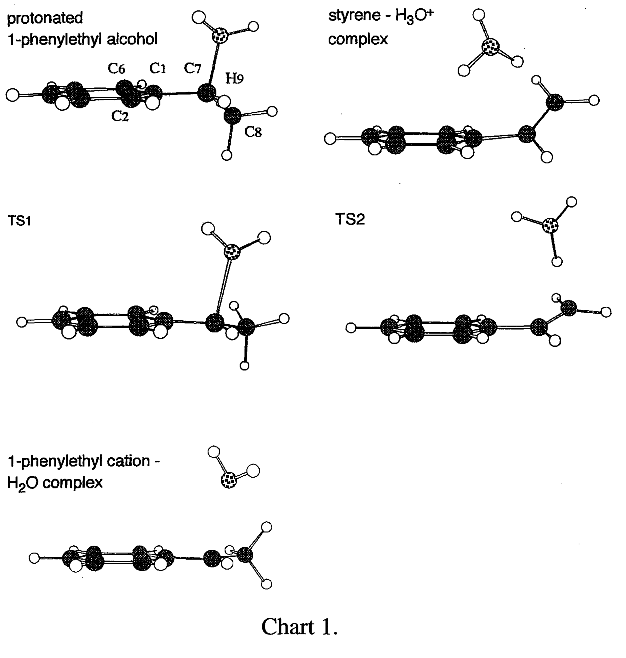


Chart 1.

The TS of the S_N1 reaction has a reaction-coordinate frequency (160i cm^{-1}) corresponding to the C_7–O stretching mode. The transition structure shows intermediate characteristics between the reactant and the product complex in many respects. The C_7O bond length is 2.077 Å, which is in between 1.641 Å (reactant) and 2.639 Å (product complex). The C_1C_7 and C_7C_8 bonds behave in similar manners. The amount of the positive charge on the phenyl ring is 0.225, 0.367, and 0.468 for the reactant, **TS1** and the product complex, respectively. From these results it can be concluded that **TS1** lies halfway between the reactant and the product. This looks unexpected because TSs of S_N1 reactions are usually considered to resemble the products in structure. As discussed below, however, the rather early transition-state character of the present model reaction is in line with the related experimental results in solution.

Isotope Effects. Kinetic-isotope effects are one of the most reliable measures of the transition structure. In the present study, kinetic as well as equilibrium isotope effects were computed from the vibrational frequencies at MP2/6-31G*. Equilibrium isotope effects can be used to evaluate the reliability of the isotope-effect calculations. Secondary deuterium equilibrium isotope effects at α (C_7) and β (C_8) were calculated to be 1.219 and 1.205, respectively. These are quite similar to the kinetic isotope effects observed experimentally for the S_N1 solvolysis of 1-phenylethyl chloride (1.22[14)] and 1.22[15)] at 25°C). Since the TS of the S_N1 solvolysis is considered to resemble the solvolysis intermediates (1-phenylethyl cation), the excellent agreement indicates that the isotope effects calculated in the present study are reliable. The α and β-^{13}C isotope effects are small, as expected.

Kinetic carbon isotope effects cannot be used as a measure of the position of the TS along the reaction coordinate because of the contribution of the isotope effect on the reaction-coordinate vibration, even at the β position in S_N1 solvolyses.[16)] On the other hand, α- and β-deuterium kinetic isotope effects are good measures of the transition-state position, since they vary monotonically on going from the reactant to the product. The calculated α-D_1 (1.089, at C_7) and β-D_3 (1.100, at C_8) kinetic isotope effects are much smaller (40—49%) than the corresponding equilibrium isotope effects. This is consistent with the conclusion derived from the geometrical parameters that the TS lies halfway between the reactant and the product for this model S_N1 reaction.

TS Characteristics. The geometrical parameters and the kinetic isotope effects examined above should vary monotonically, though not linearly, on going from the reactant (protonated 1-phenylethyl alcohol) to the product complex, and thus give a qualitative measure of the position of the TS along the reaction coordinate. Most of these parameters showed that the TS of the model S_N1 reaction lies halfway along the reaction coordinate. However, there is one exception, the coplanarity between the phenyl ring and the ethyl moiety. The coplanarity of the two moieties may be measured conveniently by the average of the two dihedral angles,

$C_8C_7C_1C_6$ and $H_9C_7C_1C_2$. These angles are −37.2°, 8.3°C for the reactant, −13.6, 8.2° for TS1, 0.5°, 2.3° for the product complex, and 0.0°, 0.0° for the isolated cation, and thus the average is 14.5°, 2.7°, 1.4°, and 0.0°, respectively. It should be noted that although the TS lies only halfway along the reaction coordinate the phenyl and ethyl moieties are almost coplanar in the TS. Since the TSs of S_N1 solvolyses of benzylic chlorides in solution are considered to more resemble the carbocation intermediates and even better coplanarity is expected in the TS, it is reasonable that the efficiency of the π-delocalization of the positive charge in the solvolysis TSs is the same as that in the intermediate cations, as listed in Table 1.[6] It should also be pointed out that the similarity of the π-delocalization does not necessarily mean that the reaction has a very late TS.

The acid-catalyzed hydrolysis of 1-phenylethyl alcohol was experimentally studied in detail.[17] On the basis of an analysis of the rate constants in 50:50 2,2,2-trifluoroethanol: water (v:v) of the C–O bond cleavage of a series of ring-substituted protonated 1-phenylethyl alcohols and of the C–O bond formation of 1-phenylethyl cations, the position of the TS for the C–O bond cleavage was estimated to be 58% with respective to the substituent-inductive effect and 47% with respective to the resonance effect. These values agree qualitatively with the present calculations, which show that the TS lies halfway along the reaction coordinate. The fact that the calculated results on the gas-phase reaction are in line with the experimental results in solution suggests that the TS characteristics are properly described by the calculation.

Hydration. Geometrical Features. Although the 1-phenylethyl cation moiety in the product complex has a geometry very similar to the isolated 1-phenylethyl cation, the geometry of the styrene moiety in the initial styrene–H_3O^+ complex is slightly different from serene, itself. The C_7C_8 double bond and the C_1C_7 bond are longer and the average dihedral angle between the phenyl ring and the vinyl plane is larger (37.2°) than that of styrene (26.2°). One of the hydrogens in H_3O^+ lies on the C_7C_8 double bond and another on the C_1C_2 double bond of the phenyl ring. This adduct ion may be regarded as a π-complex of styrene and oxonium ion, as noted by Taft many years ago.[18] The energy of the styrene–H_3O^+ adduct ion is 30.7 kcal mol^{-1} lower than that of styrene + H_3O^+.

The transition state (**TS2**) connecting the styrene–H_3O^+ complex and the product complex has a reaction-coordinate frequency (132i cm^{-1}) that corresponds mainly to the C_8–H stretching mode. The geometry shown in Chart 1 and Table 1 indicates that the lengths of the two bonds, C_1C_7 and C_7C_8, in **TS2** are more similar to those of styrene than those of the 1-phenylethyl cation. The degree of proton transfer at **TS2** on going from the styrene–H_3O^+ to the 1-phenylethyl cation–H_2O complexes is half. The positive charge on the phenyl ring in **TS2** is again closer to that of the styrene–H_3O^+ complex than that of the 1-phenylethyl cation or the cation–H_2O complex. All of these characteristics show that **TS2** lies halfway or earlier along the reaction coordinate.

Isotope Effects. The calculated β-D_2 secondary deuterium equilibrium isotope effect at C_8 ($PhCH{=}CD_2 \longrightarrow PhCH^+{-}CHD_2$) and the α-D_1 effect at C_7 ($PhCD{=}CH_2 \longrightarrow PhCD^+{-}CH_3$) are 0.911 and 0.979, respectively. These values are compared with the equilibrium isotope effects estimated from the fractionation factors compiled in the literature.[19] The fractionation factor for the secondary β-D_2 effect for a process, $CH_2{=}CD_2 \longrightarrow CH_3CHD_2$, gives K_H/K_D of 0.853. Although the β-D_2 isotope effect for the process $CH_3CHD_2 \longrightarrow CH_2^+{-}CHD_2$, is not known, this would be of a positive value, since a positive charge on the adjacent carbon atom tends to loosen the C–D bond. Thus, the β-D_2 equilibrium isotope effect for the protonation of the C=C double bond would be 0.853 or smaller (closer to unity), and agreement between the fractionation factor and the calculated β-D_2 is acceptable. The combination of the fractionation factor for $CH_2{=}CHD \longrightarrow CH_3CH(Cl)D$ (0.84) and the α-D_1 isotope effect for the limiting solvolysis of $PhCD(Cl)CH_3$ of 1.15[14] gives an estimation for the α-D_1 effect at C_7 of 0.97, which agrees well with the calculated inverse effect (0.979). Although we could not obtain a reliable estimate of the equilibrium isotope effects for other positions in the literature, the calculated isotope effects are reasonable for the proton-transfer process; the β-D_1 effect for the transferring hydrogen is slightly inverse, which is consistent with the process $O^+{-}D \longrightarrow C{-}H$,[20] and the carbon-isotope effects are small, as expected.

A comparison of the kinetic and equilibrium β-D_2 isotope effects (0.986 and 0.911) obtained in the present calculations suggests that the TS of the acid-catalyzed hydration lies early along the reaction coordinate. The conclusion is in line with the variations of the bond lengths and of the charge distribution mentioned above. A similar comparison using α-D_1 isotope effects is unreliable due to the smaller magnitudes of the effects.

TS Characteristics. We now examine the coplanarity between the phenyl ring and the vinyl moiety, which is directly related to the efficiency of the π-delocalization at TS2 and then to the magnitude of the r^+ value in the Yukawa–Tsuno equation. As in the case of the model S_N1 reaction, the extent of coplanarity is measured by the average of the two dihedral angles, $C_8C_7C_1C_6$ and $H_9C_7C_1C_2$. The value of 17.8° in TS2 is 48% of 37.2° in the styrene–H_3O^+ complex and 68% of 26.3° in styrene. It is concluded that all characteristics, including the bond length, charge distribution, isotope effect, and π-delocalization, show that **TS2** lies halfway or earlier along the reaction coordinate. Thus, all variables are synchronous in the hydration reaction.

Linear Free-Energy Relationship and Transition Structure. It is now clear that there is a distinct difference in the transition structure for S_N1 and hydration, although both processes give the same carbocation intermediate. Namely, the α-carbon center and the phenyl ring are close to coplanar in the S_N1 TS, whereas the C_α–Ph bond is twisted by about 18° in hydration. Since the coplanarity is directly related to the efficiency of the π-delocalization of the positive charge into the benzene π-system, any deviation from coplanarity should cause a decrease in the r^+ value.

A remarkably reduced r^+ value observed for solvolysis of the highly crowded benzylic system, e.g., $r^+ = 0.26$ for the α,α-di-*t*-butylbenzyl system, is a typical example for such a deviation.[21] Thus, the experimentally observed smaller r^+ value for the acid-catalyzed hydration of α-methylstyrene than for the S_N1 hydrolysis of 1-phenylethyl chloride is concluded to arise from the less-efficient coplanarity in the hydration (proton-transfer) transition structure.

The high coplanarity in the S_N1 transition structure is rationalized by the effective π-orbital overlap between the phenyl ring and the cation center, even at an early stage of the reaction. In contrast, in the hydration TS the incipient vacant π-orbital at C_7 interacts not only with the phenyl ring, but with the reacting orbital at the C_8 position; therefore, the interaction between the π-orbitals at the phenyl ring and at C_7 becomes maximum only when the proton transfer completes.

Another important conclusion obtained from the present study is that the experimentally derived r^+ value reflects the conformation of the transition structure, and thus the efficiency of the π-orbital interaction between the phenyl ring and the reaction center. In other words, the r^+ value is not necessarily related to the position of the TS along the reaction coordinate.

Epilog. A criticism often raised concerning calculations in the gas phase is that the results of such calculations are not relevant to a reaction in solution, because of the lack of medium effects. In the present study, however, medium effects are judged to only little affect the qualitative conclusions derived from the gas-phase calculations for two reasons. First, the results for closely related reaction systems are compared in this paper, and the relative characteristics of the two related TSs would be qualitatively reliable without medium effects. Second, the inclusion of a medium effect is expected to make the S_N1 reaction more endothermic, as is observed experimentally in solution,[17] and to shift the TS to be more product like. The conclusion of a nearly planar TS obtained from gas-phase calculations should be retained in a more product-like TS in solution.

A practical method used to incorporate the solvent effect in a calculation would be Monte-Carlo simulations, in which both the bulk solvent effect and the specific interaction between the substrate and solvent along the reaction path can be evaluated. We plan to perform such calculations in the near future.

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