# Determinations of Reactivity by Molecular Orbital Theory. Part 52.[1] Theoretical Studies of Solvent Effects on the Decarboxylation of 2-Cyanoacetic Acid

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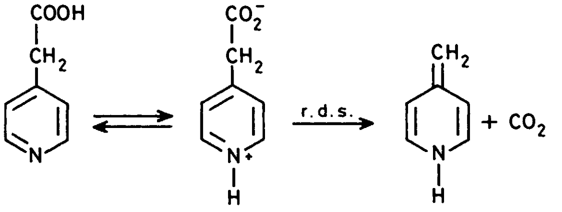
Solvent effects on the decarboxylation of 2-cyanoacetic acid in $H_2O$ and $CH_3CN$ have been investigated by means of MO calculations using the AM1 method. Four regions around the substrate molecule were identified as the probable primary solvation shell. Water was found to solvate essentially by hydrogen-bonding while acetonitrile had mainly a polarization effect in solvation. Both solvate molecules stabilized the zwitterionic form causing the elevation of activation barriers, the effect being markedly greater for water. Solvation caused shortening of the bond length and an increase in the bond order of the C–C bond which is cleaved in decarboxylation. The entropy term, $T\Delta S^{\ddagger}$, became increasingly favourable with an increase in the temperature for reaction in solution. Lower barriers were found after the main activation barrier along the reaction co-ordinate due to solvent reorganization.

The solvent has profound effects on reactivities and the mechanisms of reactions in solution by differentially solvating reactants and transition state (TS). It is well known that the rate retardation of an $S_N2$ reaction involving ionic reactants in solution is due to the preferential stabilization by solvation of the reactants over the more charge-delocalized TS. In solvation, two types of forces operative between solute and solvent are important: a non-specific dispersion force and a specific hydrogen-bonding force.[2] The former prevails in dipolar aprotic solvents while the latter predominates in protic solvents.

Recently Marlier and O'Leary have reported their experimental results for the solvent dependence of the decarboxylation rate of 4-pyridylacetic acid in dioxane–water [reaction (1)].[3] They showed that decarboxylation of the zwitterionic intermediate is the rate-determining step (r.d.s.) and the rate retardation caused by an increase in the water content is attributed to variation in the degree of TS solvation with only small changes in ground-state effects.

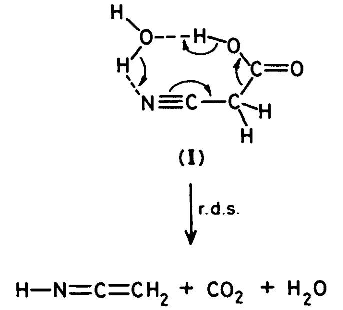


(1)

In this work, in order to carry out a theoretical study of the solvent effects involved in reaction (1), we adopted the decarboxylation of 2-cyanoacetic acid as a model and the AM1 MO calculations[4] on solvent effects using water and acetonitrile as the protic and dipolar aprotic solvent, respectively. We investigated, in some detail, various solute–solvent interactions involved, such as hydrogen-bonding, polarization involving σ-lone pairs of solvents, ion–dipole forces, and dipole–dipole forces.

## Calculations

With regard to the involvement of solvent molecules, mechanisms (2) and (3) are conceivable for the decarboxylation of 2-cyanoacetic acid.



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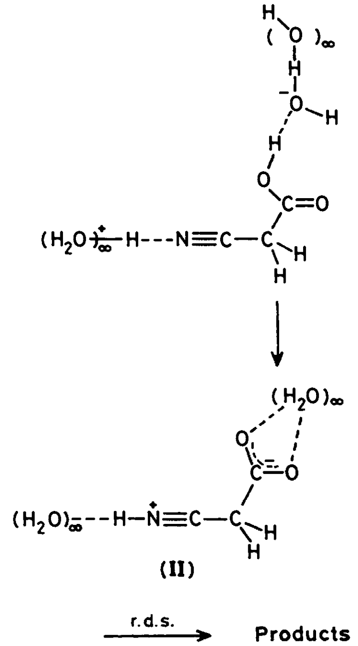
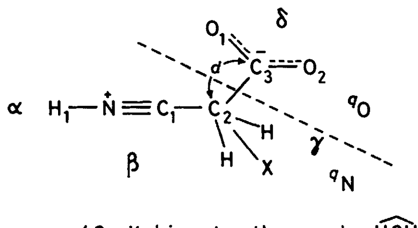


(3)

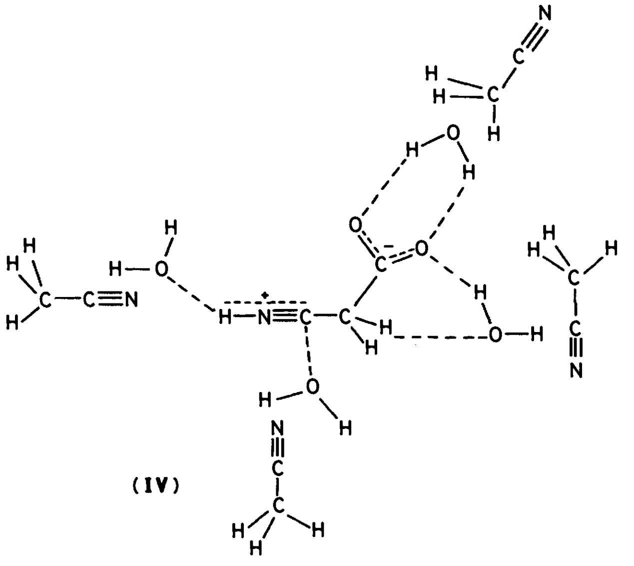
The solvent isotope effect for reaction (1)[3] was found to be unity, so that proton transfer concerted with the decarboxylation step is unlikely. Thus the reaction can be safely assumed to occur through the zwitterionic intermediate (II) and give rise to neutral decarboxylation products [equation (3)]. We therefore decided to investigate the solvent influence on the zwitterionic form (II) as the starting point.

We used the AM1 method[4,5] throughout. The $N^+$ centre in (II) develops a small degree of $sp^2$ character, whereas a strong,



(C - X bisects the angle $\widehat{HCH}$)

(III)



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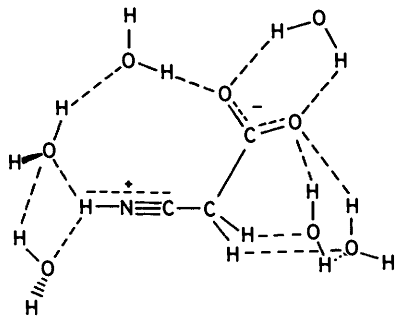


(V)

linear complex, (water)$\cdots$ $H\text{–}\overset{+}{N}\equiv C\text{–}$, is expected in solution due to the effect of the hydrogen-bonded network of the bulk water system on the terminal hydrogen. Thus we adopted a linear structure at $N^+$, H$\cdots$ $\overset{+}{N}\equiv C$–, in order to simulate the solution-phase behaviour (structural changes due to solvation are discussed below). Accordingly, we have fully optimized all geometries except this linear part of the $N^+$ centre, and the TS was located by the usual gradient norm minimization method. The diagonalized Hessian matrices had one and two negative eigenvalues for the ground state (**II**) and TS, respectively, due to this forced linearity of the $N^+$ centre in the optimization. However, the size of the negative eigenvalues was very small and indeed negligible for the ground state (**II**), while for the TS one of them was 10—20% of that for the reaction co-ordinate.

From the point of view of the co-ordination of solvent molecules with solute, there are two types of solvation: primary or chemical solvation and secondary or physical solvation. To simplify the calculations we deal only with primary solvation, *i.e.*, the first co-ordination sphere.

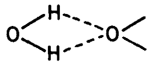
In order to identify locations of solvating molecules around the ground-state zwitterion, we have assigned four regions, α—δ. The length of the C–C bond which is breaking in the rate-determining step was designated as *d*, and charges of the fragments $CO_2$ and $HNCCH_2$ were represented as $q_O$ and $q_N$ respectively, as shown in (**III**).

The four systems we studied are: (i) no solvent; (ii) $1H_2O$ or $1CH_3CN$ at one site, α, β, γ, or δ [(**IV**)]; (iii) $3H_2O$ (α, γ, and δ); and (iv) $6H_2O$ [(**V**)].

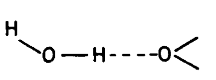
## Results and Discussion

*Structures.*—(A) *Substrate.* The atoms in (**III**) are all coplanar except the two hydrogens on carbon, so that π-electrons can delocalize over the entire zwitterion including a pseudo-π-bond formed by the two out-of-plane hydrogens.

(B) *Water co-ordination.* Theoretically two types of water co-ordination have been found: bifurcated (**VI**) and linear (**VII**) forms. The linear form maximizes attractive force while minimizing repulsion, and is more stable.[6] However, the AM1 method gives the bifurcated water dimer as the more stable form, albeit that the energy difference is very small.* In this work, no bifurcated form of water co-ordination was found in the initial solvation structure of the model system, but in a later stage of the reaction after the TS formation, bifurcated forms were encountered and accordingly a small energy barrier (0.1—0.2 kcal mol$^{-1}$) due to solvent reorganization appeared. Structures of the solvated systems are also dependent on the lone pair–lone pair repulsion, hydrogen bonding between water molecules, and π-hyperconjugation[7] of structure (**VIII**).



(VI)



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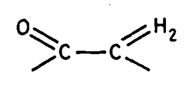

(VIII)

(C) *Structural changes due to solvation.* Comparison of the geometries in Table 1 for the solvent-free form of (**III**) with those of the $3H_2O$- and $6H_2O$-solvated forms reveals substantial structural changes occurring with solvation. In the solvent-free state, the zwitterionic nature of (**III**) is quite unstable and the structure becomes more product-like: (i) $\widehat{OCO}$ 136.44° is greater than the normal $sp^2$ angle; (ii) *d* 1.6963 Å is much longer than the normal C–C bond; (iii) $\widehat{CCX}$ of 134.06° indicates an increase in the $sp^2$ character of the carbon centre; (iv) the N–H(1) bond length is 0.9729 Å, and tends to increase with solvation.

The structural changes accompanied with solvation are: (i) $\widehat{OCO}$ decreases while C–O bond length increases; (ii) bond length *d* decreases to 1.5888 and 1.5653 in $3H_2O$- and $6H_2O$-solvated systems respectively; (iii) $\widehat{CCX}$ as well as $\widehat{HCH}$ decreases while $\widehat{CCC}$ increases; (iv) the protonic character of H(1) in the N–H(1) bond increases (Table 2) since the N–H(1) bond length increases to 0.9853 and 1.0038 Å in $3H_2O$- and $6H_2O$-solvated systems respectively. Reference to Table 2 reveals that, overall, the dispersed charge in the solvent-free system becomes localized on the $CO_2$ group and structural changes follow accordingly in the solvated systems. Extension of this trend to the bulk solvent system will lead to the localized negative charge on $CO_2$ group which will be in a rapid proton-transfer equilibrium with the bulk solvent, while the nitrogen atom,

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* The bifurcated form was found to be more stable than the linear structure by 1.89 kcal mol$^{-1}$.

**Table 1.** Geometries of the ground state (III) and TSs

| Parameter | Solvent-free |  | $3H_2O$-solvation |  | $6H_2O$-solvation |  |
|---|---|---|---|---|---|---|
|  | (III) | TS | (III) | TS | (III) | TS |
| C(1)C(2) | 1.3999 | 1.3931 | 1.4238 | 1.3790 | 1.4301 | 1.3734 |
| C(2)C(3) | 1.6963 | 1.7350 | 1.5888 | 1.8950 | 1.5653 | 1.9910 |
| C(3)O(1) | 1.2381 | 1.2341 | 1.2526 | 1.2248 | 1.2564 | 1.2172 |
| C(3)O(2) | 1.2312 | 1.2278 | 1.2484 | 1.2205 | 1.2559 | 1.2204 |
| C(1)N | 1.1673 | 1.1684 | 1.1620 | 1.1700 | 1.1600 | 1.1699 |
| NH(1) | 0.9729 | 0.9723 | 0.9853 | 0.9784 | 1.0038 | 0.9928 |
| C(2)H | 1.1154 | 1.1134 | 1.1244 | 1.1083 | 1.1284 | 1.1063 |
| C(1)$\hat{C}$(2)C(3) | 108.86 | 108.64 | 109.34 | 107.04 | 109.54 | 106.40 |
| C(2)$\hat{C}$(3)O(1) | 112.89 | 112.13 | 116.14 | 110.29 | 117.72 | 109.98 |
| O(1)$\hat{C}$(3)O(2) | 136.44 | 138.26 | 129.02 | 142.50 | 126.47 | 144.94 |
| C(1)$\hat{C}$(2)X | 134.06 | 136.13 | 128.36 | 141.91 | 127.74 | 146.09 |
| H$\hat{C}$(2)H | 112.05 | 112.67 | 108.47 | 113.00 | 108.42 | 114.63 |

Bond length in Å, bond angle in degrees.

**Table 2.** Charge for the ground state (III) (a.u.)

| Charge | Solvent-free | $3H_2O$-solvation | $6H_2O$-solvation |
|---|---|---|---|
| C(1) | 0.368 | 0.348 | 0.307 |
| C(2) | −0.360 | −0.267 | −0.256 |
| C(3) | 0.408 | 0.375 | 0.380 |
| O(1) | −0.477 | −0.532 | −0.555 |
| O(2) | −0.412 | −0.486 | −0.530 |
| N | −0.237 | −0.184 | −0.152 |
| H(1) | 0.364 | 0.390 | 0.407 |
| H | 0.172 | 0.183 | 0.195 |

which loses negative charge gradually with increasing solvation (Table 2), will form a relatively weak $H{-}N^+$ bond with a proton in the solvent. Thus, in reality, the probable mechanism in solution will be similar to process (3) above with a linear $H\cdots\overset{+}{N}{\equiv}C{-}$ structure.

*Reactivities.*—Parameters relevant to solvation effects on reactivities are summarized in Tables 3 and 4. Inspection of these Tables shows that a decrease in $d$ with solvation is accompanied by an increase in bond order or overlap population which causes an elevation of activation barrier, $\Delta H_f^{\ddagger}$, since the bond C(2)–C(3) becomes more difficult to break. When the solvation increases to $3H_2O$ and $6H_2O$, the effect becomes greater. The solvation not only results in a decrease in $d$ in the ground state (III), but also brings about an increase in bond-stretch, $\Delta d^{\ddagger}$, to achieve the length in the TS. Another important change accompanying with solvation is charge transfer from the $HNCCH_2$ fragment to the $CO_2$ group. The negative charge on the $CO_2$ group, $q_O$, increases with solvation due to this charge transfer from the $HNCCH_2$ fragment; as a result less charge transfer is needed for activation, and hence $\Delta q_O^{\ddagger}$ becomes more positive.

The dependence of the activation barrier, $\Delta H_f^{\ddagger}$, on $d$ and $\Delta d^{\ddagger}$ is shown in Table 3. The increase in $\Delta H_f^{\ddagger}$ with increases in $\Delta d^{\ddagger}$ and $\Delta q_O^{\ddagger}$ is an indication that the solvation effect accords with the Hammond postulate,[8] since the higher the activation barrier, the later is the TS along the reaction co-ordinate.

For the $CH_3CN$-solvated systems, $\Delta H_f^{\ddagger}$ values were relatively low compared with the $H_2O$-solvated sysems, in agreement with a faster rate in dipolar aprotic solvents observed experimentally for reaction (1). This is due to the smaller steric factor (or a two-centre term), $\Delta(V_{nn} - V_{ee})^{\ddagger}$, for the $CH_3CN$-solvated system than for the $H_2O$-solvated system. Energy components of the activation barrier, the one-electron term $\Delta(2\Sigma\varepsilon_i)^{\ddagger} = \Delta E_1^{\ddagger}$ and the steric factor $\Delta(V_{nn} - V_{ee})^{\ddagger} = \Delta E_2^{\ddagger}$ with $\Delta E^{\ddagger} = \Delta E_1^{\ddagger} + \Delta E_2^{\ddagger}$, are shown in Table 5. In all cases, the positive $\Delta E_2^{\ddagger}$ value predominates over the negative $\Delta E_1^{\ddagger}$, so that the steric factor controls the overall barrier height, $\Delta E^{\ddagger} = \Delta H_f^{\ddagger}$. Although the magnitude of both components, $|\Delta E_1^{\ddagger}|$ and $|\Delta E_2^{\ddagger}|$, increases with solvation, the latter increases more than the former so that the effect of solvation on $\Delta H_f^{\ddagger}$ is determined largely by the steric factor.

Qualitatively, variations of energy barriers should be approximately linear with the bond order, and hence inversely with $d$, but for the $H_2O$-solvated systems $\Delta H_f^{\ddagger}$ was found to be a quadratic function of both $d$ and $\Delta d^{\ddagger}$. Relatively stronger solvation by $H_2O$ seems to result in a larger increase in $\Delta E_2^{\ddagger}$, giving greater overall activation barrier $\Delta H_f^{\ddagger}$ compared with the corresponding $CH_3CN$-solvated systems. This enhancement of solvation effect on $\Delta E_2^{\ddagger}$ (and hence on $\Delta H_f^{\ddagger}$) produces in the $H_2O$-solvated systems a parabolic dependence of $\Delta H_f^{\ddagger}$ on bond order (and hence on $d$).

Solvation energy and the entropy factor are also expected to be important in determining reactivities, which will now be discussed.

(A) *Solvation Energy.*—The factors influencing solvation energy[9] are: (i) cavitation energy to make a hole for the substrate, (ii) orientation energy if other dipolar solvent molecules are involved around a solvated supermolecule, (iii) isotropic interaction energy corresponding to unspecific intermolecular forces, (iv) anisotropic interaction energy due to hydrogen bonding, and (v) solvation numbers depending on solvent types. In the theoretical treatment of solvation energy, the supermolecule approach[10] is often used. In this method, one first determines a solute–solvent binding mode for a solvent molecule by considering its lability and obtains a primary solvation shell. The activation energy is then determined in terms of solvation energy changes with changes in the optimal arrangement along the reaction co-ordinate. Solvation normally alters the energy profile of a reaction involving ionic reactants; the activation barrier increases due to the differential stabilization of the ground state relative to the more charge-dispersed TS. Furthermore, motions of solute and solvent also contribute to the solvation energy.

Calculated solvation energies (SE) are summarized in Table 6. Solvation shell heat of formation was computed for a structure obtained by removing the zwitterion from the solvated supermolecule, leaving behind the solvation shell around the cavity formed. The solvation energy (SE) is then given by the difference in the two energies as, SE = $\Delta H_f$(supermolecule) − [$\Delta H_f$(solvation shell) + $\Delta H_f$(substrate)]. Comparison of

**Table 3.** Enthalpies of formation ($\Delta H_f$) and of activation ($\Delta H_f^{\ddagger}$) and changes in $d(\Delta d^{\ddagger})$ and in charge $q_O$ of $CO_2$ fragment ($\Delta q_O^{\ddagger}$) in the activation of the decarboxylation reaction (3)

| Solvent | $\Delta H_f$ | $\Delta H_f^{\ddagger}$ | $d$ | $\Delta d^{\ddagger}$ | $q_O$ $(= -q_N)$ | $\Delta q_O^{\ddagger}$ $(= -\Delta q_N^{\ddagger})$ |
|---|---|---|---|---|---|---|
| Free | −7.54 | 0.01 | 1.696 | 0.039 | −0.480 | 0.037 |
| $1H_2O$ (α) | −74.59 | 0.64 | 1.651 | 0.153 | −0.543 | 0.145 |
| (β) | −70.73 | 1.03 | 1.635 | 0.187 | −0.561 | 0.178 |
| (γ) | −74.12 | 1.19 | 1.632 | 0.198 | −0.562 | 0.186 |
| (δ) | −74.33 | 1.78 | 1.620 | 0.222 | −0.579 | 0.210 |
| $3H_2O$ | −208.85 | 5.48 | 1.589 | 0.306 | −0.642 | 0.271 |
| $6H_2O$ | −417.54 | 11.80 | 1.565 | 0.426 | −0.705 | 0.361 |
| $1CH_3CN$ (α) | 6.44 | 0.64 | 1.645 | 0.159 | −0.548 | 0.152 |
| (β) | 6.99 | 0.96 | 0.637 | 0.187 | −0.562 | 0.177 |
| (γ) | 7.96 | 0.51 | 1.647 | 0.152 | −0.546 | 0.147 |
| (δ) | 8.02 | 0.96 | 1.636 | 0.184 | −0.559 | 0.175 |

$\Delta H_f$ and $\Delta H_f^{\ddagger}$ in kcal mol$^{-1}$, $d$ and $\Delta d^{\ddagger}$ in Å, and $q_O$ and $\Delta q_O^{\ddagger}$ in a.u.

**Table 4.** Bond order and overlap population of the C(2)–C(3) bond in the ground state (**III**)

| Solvent | Bond order | Overlap population |
|---|---|---|
| Free | 0.5150 | 0.9994 |
| $1H_2O$ (α) | 0.5797 | 1.1703 |
| (β) | 0.5996 | 1.2369 |
| (γ) | 0.6068 | 1.2497 |
| (δ) | 0.6260 | 1.3027 |
| $3H_2O$ | 0.6917 | 1.4662 |
| $6H_2O$ | 0.7531 | 1.6076 |
| $1CH_3CN$ (γ) | 0.5832 | 1.1856 |
| (α) | 0.5859 | 1.1919 |
| (δ) | 0.5989 | 1.2320 |
| (β) | 0.5998 | 1.2274 |

**Table 5.** Energy components for activation barriers ($\Delta H_f^{\ddagger} = \Delta E^{\ddagger}$) (eV) of the decarboxylation reaction (3)

| Solvent | $\Delta(2\sum_{i}^{occ}\varepsilon_i)^{\ddagger} = \Delta E_1^{\ddagger}$ | $\Delta(V_{nn} - V_{ee})^{\ddagger} = \Delta E_2^{\ddagger}$ | $\Delta E^{\ddagger} = \Delta E_1^{\ddagger} + \Delta E_2^{\ddagger}$ |
|---|---|---|---|
| Free | −0.781 | 0.782 | 0.0003 |
| $1H_2O$ (α) | −1.001 | 1.029 | 0.028 |
| (β) | −2.225 | 2.270 | 0.044 |
| (γ) | −4.576 | 4.627 | 0.051 |
| (δ) | −8.165 | 8.242 | 0.077 |
| $3H_2O$ | −9.464 | 9.702 | 0.238 |
| $1CH_3CN$ (γ) | −4.051 | 4.074 | 0.022 |
| (α) | −1.283 | 1.311 | 0.020 |
| (δ) | −7.828 | 7.870 | 0.041 |
| (β) | −1.224 | 1.265 | 0.041 |

**Table 6.** Solvation energies for the ground state (**III**) (GS) and changes in solvation energies [$\Delta(SE)^{\ddagger}$] in the activation (kcal mol$^{-1}$) of the decarboxylation reaction (3)

| $H_2O$ | SE(GS) | $\Delta(SE)^{\ddagger}$ | $CH_3CN$ | SE(GS) | $\Delta(SE)^{\ddagger}$ |
|---|---|---|---|---|---|
| (α) | −7.813 | 0.630 | (γ) | −3.776 | 0.500 |
| (β) | −3.948 | 1.019 | (α) | −5.293 | 0.625 |
| (γ) | −7.342 | 1.176 | (δ) | −3.716 | 0.949 |
| (δ) | −7.543 | 1.767 | (β) | −4.748 | 0.951 |
| $3H_2O$ | −23.767 | 5.561 | | | |
| $6H_2O$ | −48.115 | 13.407 | | | |

**Table 7.** Charges of the solvents (a.u.) in the ground state (**III**)

| Solvent site | α | β | γ | δ |
|---|---|---|---|---|
| $1H_2O$ | 0.0119 | −0.0012 | −0.0095 | −0.0099 |
| $1CH_3CN$ | 0.0130 | 0.0003 | −0.0004 | −0.0029 |

activation barriers, $\Delta H_f^{\ddagger}$, in Table 3 with solvation energy of activation, $\Delta(SE)^{\ddagger}$, in Table 6 indicates that varations in the activation barrier with solvation originate largely in the solvation energy of activation. There is no direct proportionality between the (SE) and $\Delta(SE)^{\ddagger}$ values, showing that ground-state solvation effect contributes little to the solvation energy of activation, and hence to the activation barrier, as claimed by Marlier and O'Leary from experimental results for reaction (1). Our results on charge distribution in Tables 2 and 3 indicate that the role of solvent in solvation varies depending on the site of solvation. At the α, γ, and δ sites, water forms a strong hydrogen bond, while at β it solvates the solute by dipole–dipole interaction. At the γ site, however, water has the additional effect of promoting π-hyperconjugation[7] in the O=C–C=$H_2$ fragment, and the =$H_2$ part also forms hydrogen bonds with the water oxygen as a result of σ-induced dipole formation. On the other hand, $CH_3CN$ solvates at α and β by polarization since the nitrogen atom has very small charge of −0.050, and the much higher HOMO (a non-bonding MO) level of $CH_3CN$ compared with that of $H_2O$ contributes much more effectively to the orbital interaction[11] with the substrate. At the γ and δ sites, $CH_3CN$ forms hydrogen bonds but in the former there is also a dipole–dipole interaction. Besides these, one should note that we have ion–dipole interactions between solvent and solute in all cases.

Overall, water solvates mainly by hydrogen bonding, whereas acetonitrile solvates by polarization and dipole–dipole interaction, hydrogen bonding by $CH_3CN$ being of little importance. Hydrogen bonding by $H_2O$ provides a stronger solvation than the polarization by $CH_3CN$, so that the $H_2O$-solvated system has a greater effect in elevating the activation barriers mainly due to the large solvation energy of activation, $\Delta(SE)^{\ddagger}$, as can be seen in Tables 3 and 6.

There are two additional factors that should be accounted for in solvation. (i) Conductance data have shown that solvation number for $Li^+$–$CH_3CN$ system is 9, whereas it is 21 for the $Li^+$–$H_2O$ system,[12] indicating that the solvating ability of $H_2O$ is more than twice as great as that of $CH_3CN$ in solution (for the $Li^+$ cation). (ii) A zwitterionic solute should interact strongly with solvent so that secondary solvation will become important. Hence the protic solvent, $H_2O$, should interact more strongly with a zwitterionic solute with considerable increase in the solvating ability due to the secondary solvation effect. By taking all these factors into account we conclude that the difference in the solvation effects on the activation barrier between $H_2O$ and $CH_3CN$ will become much greater in the bulk solvent system than we have seen in Tables 3, 5, and 6 for the limited solvation numbers.

(B) *Entropy*.—Entropies of solvated systems will change along with changes in solvation ability. Although entropy factor, $T\Delta S^{\ddagger}$, contributes to the activation free energy, $\Delta G^{\ddagger}$, the barrier is determined mainly by enthalpy factor,* $\Delta H^{\ddagger}$, especially at room temperature, *e.g.*, $\Delta H_f^{\ddagger}$ 1.19 (Table 3) and $T\Delta S^{\ddagger}$ 0.29 kcal mol$^{-1}$ for $H_2O$ solvating at the $\gamma$ site. It was found that the solvent-free system has negative temperature dependence while the $H_2O$-solvated system has positive temperature dependence. The increase in $T\Delta S^{\ddagger}$ is, however, very small and hence the effect of entropy term should be insignificant at room temperature.

(C) *Charge Transfer*.—Inspection of Table 7 indicates that the orbital (HOMO − LUMO) interaction[11] (at $\alpha$ and $\beta$) is more important than the electrostatic interaction (at $\gamma$ and $\delta$) for charge transfer between solvent molecule and substrate; the magnitudes of charges are greater at the $\alpha$ and $\beta$ than at the $\gamma$ and $\delta$ sites. At the $\alpha$ and $\beta$ sites, the $\sigma$-lone pairs of solvent molecules participate directly in solvation. Charge transfer is more efficient with $CH_3CN$ for which the HOMO − LUMO gap is smaller than that for $H_2O$ (positive values at $\alpha$ and $\beta$ for $CH_3CN$ are greater than those for $H_2O$). This means that relatively greater amount of electronic charge transfers from solvent to solute in $CH_3CN$ than in $H_2O$ at the $\alpha$ and $\beta$ sites. On the other hand, the electrostatic interaction is dominant in the charge transfer at the $\gamma$ and $\delta$ sites; the stronger electrostatic attraction by $H_2O$ than by $CH_3CN$ seems to enhance the charge transfer from the substrate to $H_2O$ at the $\gamma$ and $\delta$ sites (negative charges at $\gamma$ and $\delta$ are greater for $H_2O$ than for $CH_3CN$).

## Acknowledgements

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* Enthalpy values calculated by semiempirical MO methods differ from experimental ones, so that absolute values are not significant.