

ligand in organic solvent is not clear as yet. From our results, however, we can deduce that the planarity of the acac ligand having dipole moment is influenced by the solvent molecules, and that the distortion of its planarity due to an interaction such as polar linkage between solvent and C-CH<sub>3</sub> group of acac is induced.

As seen in Figure 7, the CD spectrum of A-[Co(acac)<sub>2</sub>(tn)]ClO<sub>4</sub> complex in solid state bears some resemblance to the spectra in organic solvents which have low dipole moment and dielectric constant with the exception of some solvents. Thus, because of the interaction between solvents and C-CH<sub>3</sub> groups of acetylacetonate ligands, it is deduced that the conformation of coordinated acac ligands can be changed in solvents, and that the conformational changes influence on the CD spectra. The similarity of the CD spectra measured in the solvents of low polarity and that in solid indicate that the ligand conformation of the complex is similar in both states. Since a series of solvents interact with C-CH<sub>3</sub> groups of acac ligand more weakly than water, does the acac ring of complex can be less flexible, and it is deduced that the CD spectra in both states resemble each other.

In conclusion, from CD spectra analyses, it is apparent that the solvent plays an important role in the conformational change of acetylacetonate rings in [Co(acac)<sub>2</sub>(diamine)]<sup>+</sup> complexes, and that the degree of flexibility of acac rings is more affected by the dielectric constant than by the dipole moment.

**Acknowledgement.** This work was financially supported by the Basic Science Research Institute Program, Ministry of Education, Korea, 1986.

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## Theoretical Studies of Solvent Effects on Gas Phase Reactions of Methoxide Ion with Substituted Ethylenes<sup>†</sup>

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Solvent effects on gas phase reactions of methoxide ion with substituted ethylenes, CH<sub>2</sub>=CHR where R=CN,CHO and NO<sub>2</sub>, are investigated theoretically using the AM1 method. Results show that the methoxide approaches in-plane in all reactions, but subsequently rotate out-of-plane to form tetrahedral complexes in addition reactions. All reactions of a bare methoxide are found to be exothermic, the exothermicity being the greatest in the β-addition, in which the excess energy is forced to be contained within the β-adduct rendering extreme instability. However a part of the excess energy can be removed by a solvate molecule giving a stable complex prior to the product formation. The hydride transfer processes were found to be unfavorable due to the high activation barriers. The α-H<sup>+</sup> abstraction process from acrylonitrile becomes endothermic as a result of monosolvation of the methoxide, in agreement with experimental results.

### Introduction

Gas phase ion-molecule reactions have played an impor-

tant role in the elucidation of mechanisms in organic chemistry. Recently it has been shown both experimentally<sup>1</sup> and theoretically<sup>2</sup> that the removal of all solvation from reactants in ion-molecule reactions can drastically alter not only

<sup>†</sup>Determination of Reactivity by MO Theory (Part 51).

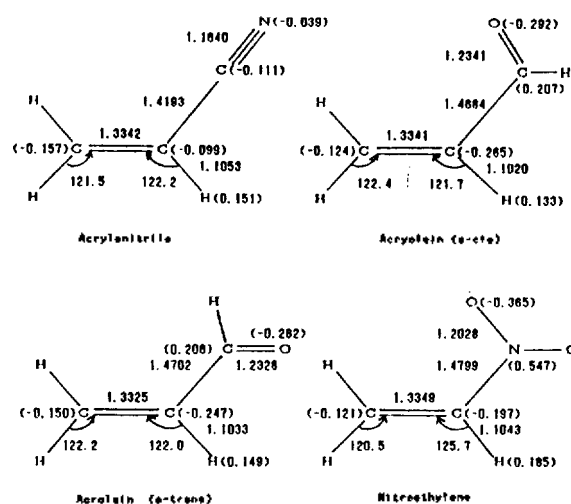


Figure 1. Geometries and charges (in parenthesis) of reactants.

their orders of reactivity but also the mechanisms by which they react. Bartmess<sup>3</sup> has reported his ICR experimental results that the gas phase reaction products of the reaction of methoxide with substituted ethylenes  $H_2C=CHR$ , such as acrylonitrile ( $R=CN$ ), acrolein ( $R=CHO$ ) and nitroethylene ( $R=NO_2$ ), depend on whether the methoxide ion is bare or monosolvated; no  $\beta$ -addition products were observed with a bare methoxide even though the addition is the principal mode of reaction in the condensed phase, while the major products with a monosolvated methoxide were found to be the  $\beta$ -adducts.

In this work, we report results of our MO theoretical studies on the gas phase reactions of the substituted ethylenes with a bare as well as monosolvated methoxide ion.

### Calculations

All calculations were carried out using the AM1 Method.<sup>4</sup> All geometries were fully optimized using standard gradient method. Stationary points and transition states (TS) were rigorously located by diagonalizing the force constant matrix.<sup>5</sup> Altogether five types, (1)~(2S), of reactions for three substrates (A~C) have been investigated:

Substrates;  $CH_2=CHR$ , where (A)  $R=CN$ ,  
(B)  $R=CHO$ , (C)  $R=NO_2$ .

Reactions; (1)  $\alpha$ -proton ( $H^+$ ) abstraction by a bare methoxide, (2)  $\beta$ -addition of a bare methoxide, (3) hydride transfer from a bare methoxide, (1S)  $\alpha$ - $H^+$  abstraction by a mono-hydrated methoxide, (2S)  $\beta$ -addition of a monohydrated methoxide.

### Result and Discussion

The optimized geometries of the reactants are summarized in Figure 1. As has been noted previously,<sup>6</sup> the AM1 method gives a bifurcated hydrogen bonding structure of  $H_2O$  in the monohydrated methoxide. Acrolein ( $R=CHO$ ) has two

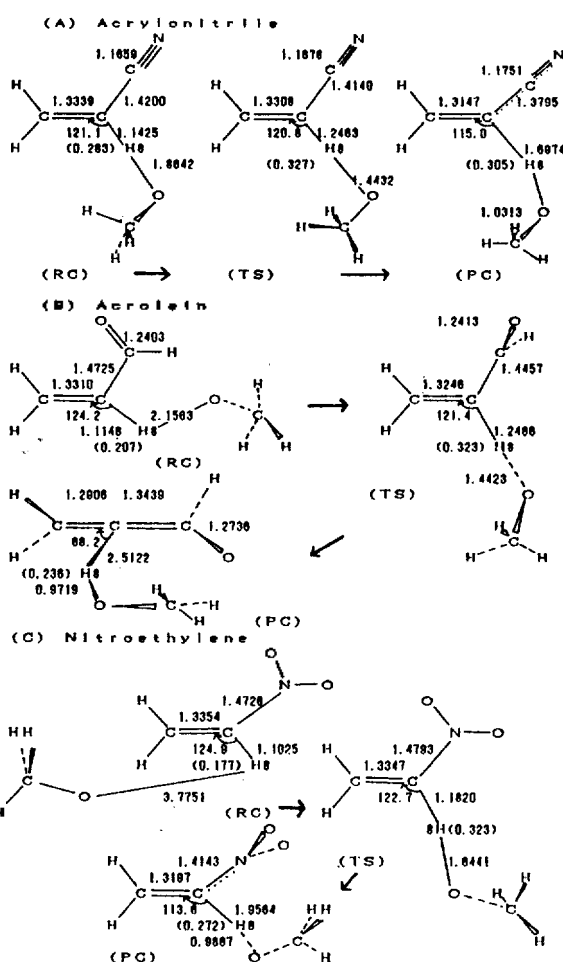
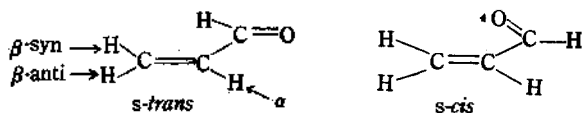
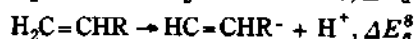


Figure 2. Geometries and charges (in parenthesis) for species on stationary points and transition states in reaction processes (1).

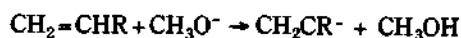
forms, *s-cis* and *s-trans*, the energies of which differ only by  $\sim 0.2$  kcal/mol with a rotational barrier of 1.5 kcal/mol. We report here only for one form since the two were similar in reactivities.<sup>7</sup> Our AM1 results have shown that of the three vinylic hydrogens, the one on the  $\alpha$ -carbon ( $\alpha$ -H) is the most acidic i.e., the  $\alpha$ -H is the easiest to cleave as a proton;



R	$\Delta E_\alpha$ (kcal/mol)	$\Delta E_\beta$ (kcal/mol)
CN	13.0	26.1
CHO	6.0	28.3
$NO_2$	-9.1	2.6

We therefore proceeded to calculate the proton abstraction from the  $\alpha$ -carbon ( $\alpha$ - $H^+$ ) only.

(1)  $\alpha$ -Proton abstraction by a methoxide



The results are exhibited in the reaction processes for the three substrates in Figure 2. The reactant complexes (RC) are formed by the methoxide oxygen approaching  $\alpha$ -H within the molecular plane (in-plane), which is pulled away as a proton in the later stage of reactions. The whole process takes

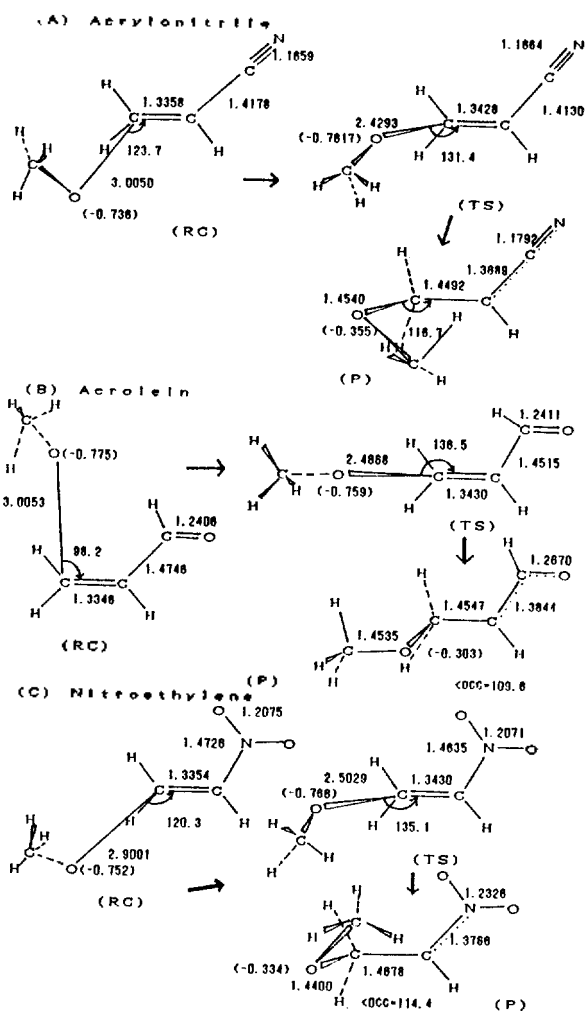
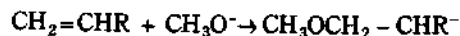


Figure 3. Geometries and charges (in parenthesis) for species on stationary points and transition states in reaction processes (2).

place in-plane. In general, bond lengths of  $C_1=C_2$  and  $C_2-R$  decrease while those of multiple bonds in R, i.e.,  $C\equiv N$ ,  $HC=O$ , and  $-N\equiv O$ , stretch as the reaction proceeds. This is due to the delocalization of the negative charge developed at  $C_2$ , achieving stabilization of the anion formed. Progressive increase in the negative charge is the greatest at a terminal heteroatom in R. The transferring hydrogen,  $\alpha$ -H, becomes most positive at the TS along reaction coordinate as one might have expected. The in-plane angle  $\angle C_1C_2R$  increases as the reaction proceeds in order to effectively conjugate the vicinal multiple bonds of the  $C_2$  atom, as the bond length changes indicate. In acrolein ( $R=CHO$ ) and nitroethylene ( $R=NO_2$ ), the terminal oxygen atom is repelled out of the molecular plane (out-of-plane) by the developing lone pair at the  $C_2$  atom which is in-plane.

#### (2) $\beta$ -addition of a methoxide



In this reaction, there is no product complex (PC) following the TS and the product is directly formed from the TS with excess energy contained in the adduct itself. The reaction processes are shown in Figure 3.

The TS is formed by the methoxide approaching olefinic  $\pi$  bond out-of-plane with an angle  $\angle OC_1C_2$  of  $131\sim 136^\circ$  at

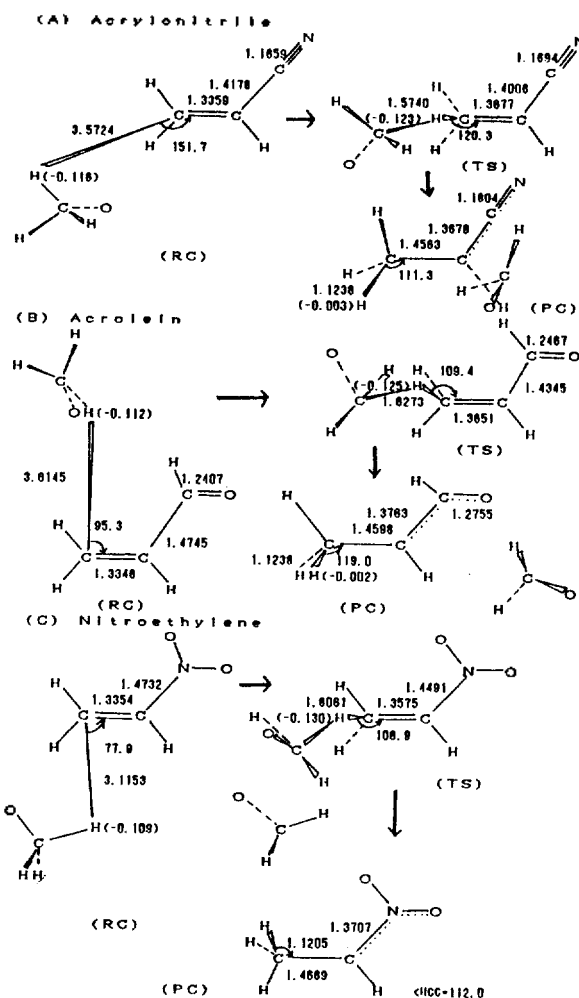
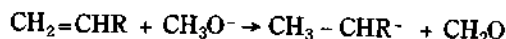


Figure 4. Geometries and charges (in parenthesis) for species on stationary points and transition states in reaction processes (3).

$C_1$ . This is somewhat greater than that obtained for the hydride attack on ethylene by the ab initio calculations.<sup>9</sup> This difference in the angle of approach could be originated in the bulky  $CH_3O^-$  ion interacting with the multiple bond in the terminal R group. Here again, the increase in the negative charge is substantial at the terminal heteroatom in R. Since the methoxide oxygen adds to the  $C_1$  atom tetrahedrally, the negative charge is delocalized over the rest of the substrate as in the  $\alpha$ -H<sup>+</sup> abstraction; thus the bond  $C_1=C_2$  is stretched while the bond  $C_2-R$  is compressed as a result of conjugation and stabilization of the anion formed.

#### (3) Hydride transfer from a methoxide



The results are presented in reaction processes in Figure 4.

The methoxide approaches in-plane forming a complex (RC) but it rotates out-of-plane in the TS so that one of the hydrogens in  $CH_3O^-$  can attack  $C_1$  tetrahedrally. The product anion is then solvated by the other product, formaldehyde  $CH_2O$ , to form a stable complex (PC). The bond length changes are again similar to those observed in reactions (1) and (2) above.

#### (1S) $\alpha$ -H<sup>+</sup> abstraction by a monosolvated methoxide

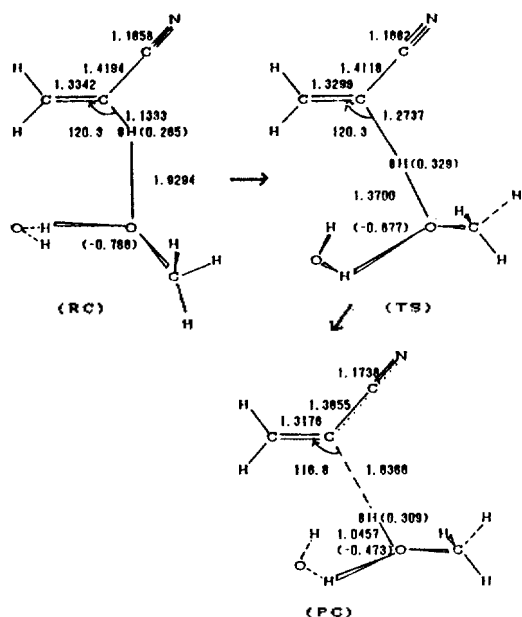


Figure 5. Geometries and charges (in parenthesis) for species on stationary points and transition states in reaction process (1S) of acrylonitrile.

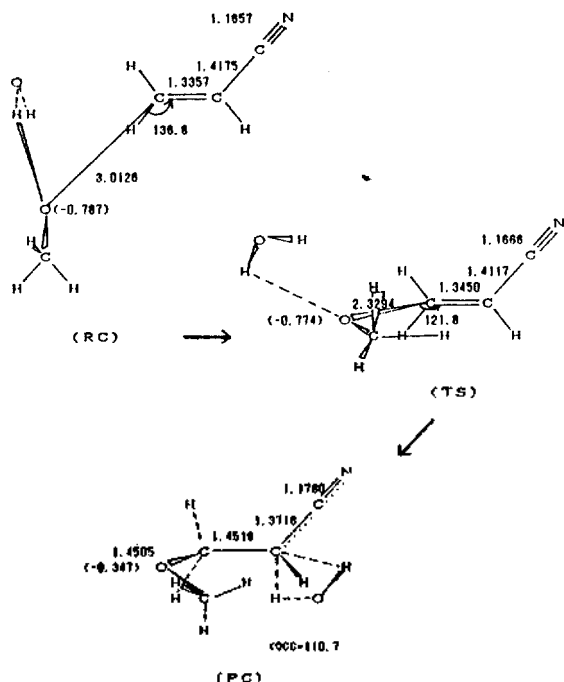
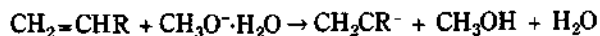


Figure 6. Geometries and charges (in parenthesis) for species on stationary points and transition states in reaction process (2S) of acrylonitrile.



The results in Figure 5 for acrylonitrile show that the structures of RC, TS and PC are similar to those of the reaction (1), except the methoxide is hydrated. In the other reactions, i.e., for R=CHO and R=NO<sub>2</sub>, the trends were the same, so that the structures of the complexes and TS were simply the hydrated types of those involved in the corresponding reactions (1) and (2) as for the R=CN shown in Figure 5.

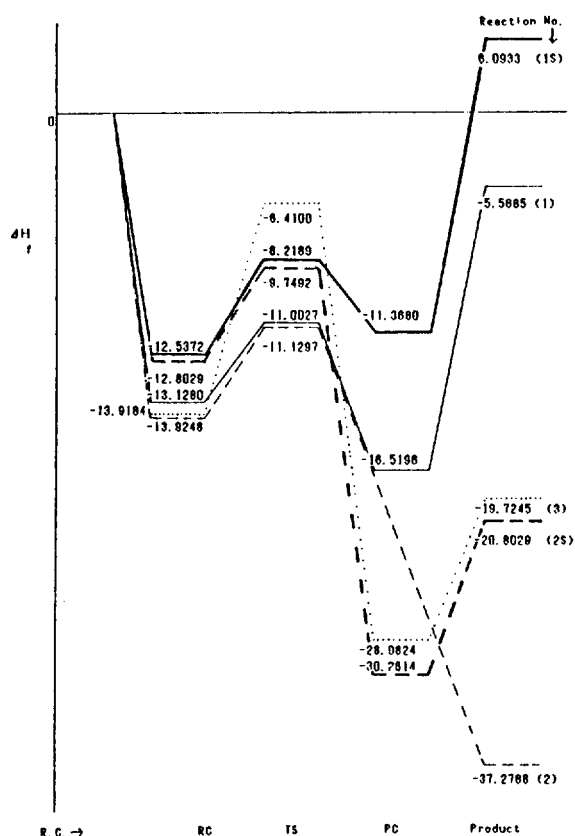


Figure 7a. Enthalpy profiles for reaction processes of acrylonitrile (R=CN).

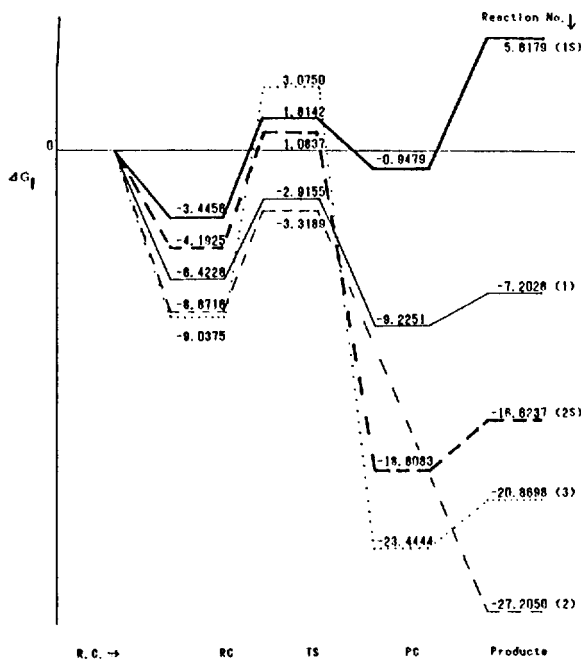
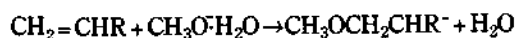


Figure 7b. Free energy profiles for reaction processes of acrylonitrile (R=CN).

However the energetics are altered drastically by a solvate water, which will be discussed subsequently.

(2S)  $\beta$ -addition of a monosolvated methoxide



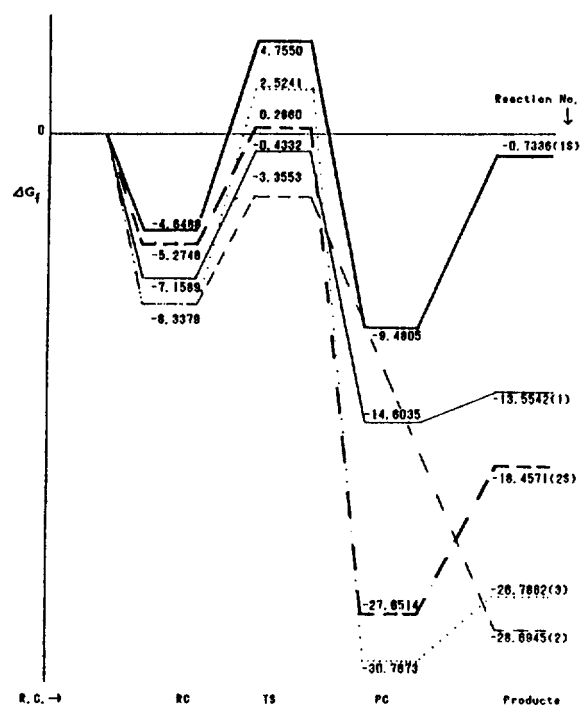


Figure 8. Free energy profiles for reaction processes of acrolein (R=CHO).

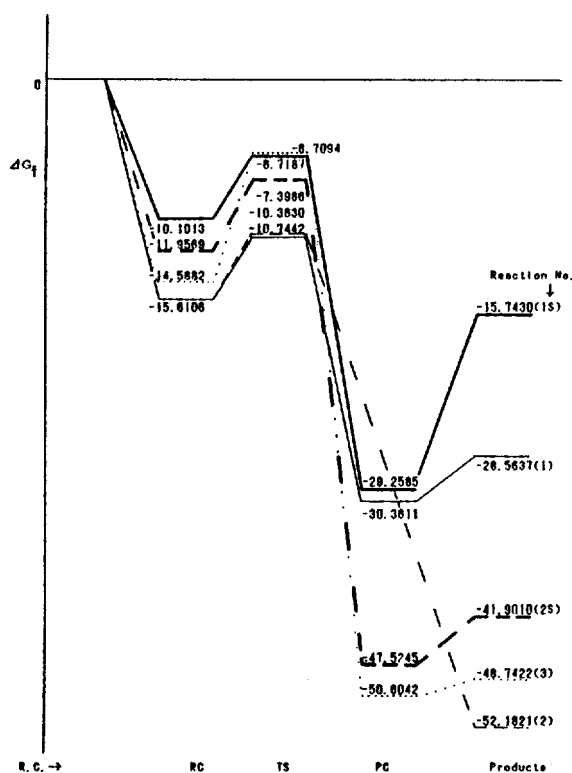


Figure 9. Free energy profiles for reaction processes of nitroethylene (R=NO<sub>2</sub>).

The results are presented in the reaction process for acrylonitrile in Figure 6. The hydrated methoxide now approaches C<sub>1</sub> with an angle of ~120° out-of-plane as required to form a tetrahedral carbon center in the product anion. The water molecule then solvate the most negatively charged car-

bon center, C<sub>2</sub>, and forms a stable complex, (PC). This is in contrast with the reaction (2), where no such product complex prior to the product formation was possible due to the lack of a solvate molecule. In this complex, the excess energy of the adduct can be partially removed by the water molecule, so that the adduct can sustain itself until the products are formed by desolvation with some expense of the energy.

## Energetics

Energy profiles are presented in Figures 7, 8 and 9 for the reactions of the three substituted ethylenes. Three reactions involving a bare methoxide, (1)~(3), yield an anionic product and are all exothermic so that the gas phase reactions should be observable experimentally.  $\alpha$ -H<sup>+</sup> abstraction by a monosolvated methoxide, (1S), is however endergonic by ~6 kcal/mol for acrylonitrile and nearly ergoneutral for acrolein, so that the gas phase reactions will not proceed as experimentally found. Inclusion of entropy factor leads to elevation of energy levels in general, the elevation being marked, however, for the TS; the reactions (1S), (2S) and (3) have energy barriers,  $\Delta G^*$ , above the ground state (reactants) level for R=CN and R=CHO (Figures 7 and 8).

The energetics are summarized in Table 1 for the three ethylenes. Reference to the Table reveals that exothermicity or exoergonicity increases in the order R=CN < CHO < NO<sub>2</sub>, which is not the order of inductive substituent constants  $\sigma_I$  for R ( $\sigma_I$ : CHO=0.31, CN=0.56, NO<sub>2</sub>=0.63)<sup>10</sup>, but is the order of anion conjugation ability of R,  $\sigma_p^-$  ( $\sigma_p^-$ : CN=0.88, CHO=1.03, NO<sub>2</sub>=1.24)<sup>11</sup>. The exothermicity, therefore, depends upon the ability to stabilize the product anion by direct conjugation of the anionic center in R with the vinylic double bond.

Reaction (2) is found to be the most exothermic process for all substrates. The large excess energy of over ~40 kcal/mole ( $\Delta H_f$  of -37, -40, and -63 kcal/mol for R=CN, CHO and NO<sub>2</sub> respectively) is carried by the adduct itself, which should render the adduct extreme instability so that it will eventually disintegrate back to the reactants or to fragments in a different manner to product. Thus the  $\beta$ -addition of a bare methoxide to CH<sub>2</sub>=CHR will not be possible as has been reported experimentally. Partial removal of the excess energy by a solvate molecule can lead to a stable product complex (PC), which will then decompose into the adduct and H<sub>2</sub>O with the expense of some energy. Thus the participation of at least one solvate molecule is essential for the gas phase  $\beta$ -addition of a methoxide ion to the substituted ethylenes to proceed.

Acrylonitrile (R=CN) has the highest activation barrier in the hydride transfer reaction (3), whereas nitroethylene (R=NO<sub>2</sub>) has large exothermicity for the same reaction (3), which will make the products unstable although part of the energy may be removed by the other product, formaldehyde. These could be the reasons why the reaction (3) was not observed experimentally in the gas phase reactions of acrylonitrile and nitroethylene. Moreover, the reaction (3) has the highest activation barrier for all ethylenes, in support of the slowest rate observed for acrylonitrile.

The results of our studies can be summarized as follows:

(1) The methoxide approaches in-plane in all reactions,

Table 1. Energetics (kcal/mol) involved in gas phase reactions of CH<sub>2</sub>=CHR with CH<sub>3</sub>O<sup>-</sup> and CH<sub>3</sub>O<sup>-</sup>·H<sub>2</sub>O

(kcal/mole) Reaction	CH <sub>2</sub> =CHCN			CH <sub>2</sub> =CHCHO			CH <sub>2</sub> =CHNO <sub>2</sub>		
	ΔH°	ΔG°	ΔG*	ΔH°	ΔG°	ΔG*	ΔH°	ΔG°	ΔG*
1	-5.6	-7.2	3.5	-12.7	-13.6	6.7	-27.6	-28.6	4.9
2	-37.3	-27.2	5.6	-39.6	-28.7	4.1	-63.2	-52.2	5.2
3	-19.7	-20.9	12.1	-26.4	-26.8	10.9	-47.9	-48.7	7.9
1S	6.1	5.6	5.3	-1.1	-0.7	9.4	-15.9	-15.7	3.4
2S	-20.8	-16.6	5.3	-23.2	-18.5	5.0	-46.7	-41.8	4.6

$$\Delta H^{\circ} = \Delta H_f(P) - \Delta H_f(R); \quad \Delta G^{\circ} = \Delta G_f(P) - \Delta G_f(R); \quad \Delta G^* = \Delta G_f(TS) - \Delta G_f(RC).$$

but subsequently rotate out-of-plane to form tetrahedral complexes in addition reactions (2 and 3).

(2) The reactions of substituted ethylenes (CH<sub>2</sub>=CHR) with a bare methoxide are all exothermic, the exothermicity being the greatest in the β-addition reaction.

(3) Although the β-addition (reaction 2) is the most exothermic process, the excess energy is carried by the adduct alone so that it becomes extremely unstable.

(4) The solvate water removes part of the excess energy in the β-addition of monosolvated methoxide to render the reaction product.

(5) The hydride transfer (3) is the most unfavorable process due to the highest energy barrier.

(6) The α-H<sup>+</sup> abstraction of acrylonitrile becomes endothermic by hydrating the methoxide ion so that the gas phase reaction will not be observed.

**Acknowledgements.** We thank the Ministry of Education and the Korea Center for Theoretical Physics and Chemistry for support of this work.

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- Water dimer had energy difference of less than 1 kcal/mol between bifurcated and linear forms.
- Geometrical changes and energetics along reaction coordinate were found to be similar for the two forms of acrolein.
- For anti-H. Results for syn-H were similar.
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- J. A. Dean ed., 'Lange's Handbook of Chemistry,' McGraw-Hill, New York., 1985, 13th ed., p. 31-140 (for phenol)

## Temperature Dependence of the Vibration-Vibration Energy Transfer in the Deexcitation of NO(2) by NO(0)

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The temperature dependence of the vibrational relaxation of NO(*v*=2) by NO(*v*=0) has been investigated over the temperature range 100-3000K. We have assumed that the deexcitation of NO(2) by NO(0) undergoes vibration-to-vibration (VV) energy exchange with the transfer of the energy mismatch Δ*E* through rotation (R) and translation (T). The relaxation rate constants are calculated by solving the time-dependent Schrödinger equation. The sum of V-V, T, and V-V,R contributions shows very weak temperature dependence and is in reasonable agreement with observed data over the temperature range 300-3000K.

### Introduction

The vibrational relaxation of NO has been studied by a

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variety of techniques. Most of these studies have involved the measurements of the relaxation rate constant of NO(*v*=1)<sup>1-4</sup> by a variety of collision partners. However, a few investigators have studied the self-relaxation of NO(*v*=2).<sup>1,5-8</sup> In this paper, we have considered the rate con-