Theoretical Studies on the Gas-phase Reaction of Methyl Formate with Anions†

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The gas-phase reactions of methyl formate with anions, $^-NH_2$, ^-OH, $^-CH_2CN$, are studied theoretically using the AM1 method. Stationary points are located by the reaction coordinate method, refined by the gradient norm minimization and characterized by the determination of Hessian matrix. Potential energy profiles and the stationary point structures are presented for all conceivable processes. Four reaction paths are found to be possible: formyl proton and methyl proton abstractions, carbonyl addition, and S_N2 process. For the most basic anion $^-NH_2$ the proton abstraction path is favored, while in other case, OH and $^-CH_2CN$, the carbonyl addition paths are favored. In all cases the S_N2 process is the most exothermic, but due to the relatively high activation barrier the process can be ruled out.

Introduction

Nucleophilic substitutions at the carbonyl carbon atom have been studied extensively in organic chemistry.[1] These reactions are of great importance, especially in solution-phase, because of their role in biochemistry. Despite the considerable activity in the mechanistic study of reactions of carbonyl groups in solution, the intrinsic factors controlling the reactivity and mechanism of carbonyl substitution have been elusive due to attendant complications of the solvent system. A number of gas phase studies of ionic nucleophilic displacement reactions at carbonyl centers using ion cyclotron resonance(ICR) spectroscopy,[2] flowing afterglow(FA) technique and fourier transform mass spectrometry(FT-MS) have been reported.[3]

The results of these gas-phase studies have shown that the reactivity and mechanism of the carbonyl substitution are substantially different from those of the solution-phase; effects of the nucleophile, leaving group and alkyl substrate on the rate are found to be inconsistent with the single minimum potential surface postulated from solution phase studies and many reaction paths are found to be possible.[4] However, the product distribution in the gas-phase reaction is strongly dependent upon the reaction condition, and this complication inherent to the gas-phase studies presented difficulties in the complete understanding. The product distribution is primarily determined by how the excess energies of the product complexes or intermediates are lost to reach equilibrium as shown in eq.(1), where k_c, k_r and k_d are the rate constants for

$$A^- + B \leftrightarrow (AB^-)^* \begin{cases} \xrightarrow{k_c[M]} AB^- \\ \xrightarrow{} AB^- + h\nu \\ \xrightarrow{k_r} \\ \xrightarrow{k_d} C^- + D \end{cases} \quad (1)$$

the energy loss of $(AB^-)^*$ by collison with a neutral gas molecule M, by radiation and by decomposition, respectively.

The gas phase reactions of methyl formate with various anions have been reported with varying product ratios depending upon the reaction conditions.[5] In order to understand and clarify the intrinsic factors determining the reaction mechanism we have carried out theoretical investigations of the gas-phase reactions of methy formate with anions of different thermodybamic properties, $^-NH_2$, ^-OH, $^-CH_2CN$, using the AM1 method

†Determination of Reactivity of MO Theory (Part, 60).

Calculations

The AM1 method[6] was used for geometries and reaction paths calculations throughout in this work. Locations and geomertries of the stationary points on the potential energy surfaces were obtained by the reaction coordinate method,[7] refined by the gradient norm minimization[8] and characterized by the force constant matrix calculation. The transition state(TS) was confirmed by only one negative eigenvalue in the Hessian matrix.[9] All geometries were fully optimized without any assumption.

Results and Discussion

Structures of Methyl Formate and Carbonions. Of the four conformers of methyl formate, the staggered-cis form is the most stable conformer as expected from favorable π-nonbonded interaction ($6\pi/5$),[10] Figure 1.

This is in agreement with the *ab initio* results of Wennerström[11] and with explanations offred by Epiotis *et al.*[12] The staggered-cis form is more stable by 5.6 and 0.6 kcal/mol than the staggered-trans and eclipsed-cis, respectively, which is in accorded with the experimental results. In this work, we used the staggered-cis form as the ground state of methyl formate.

The carbanions(A) formed by the elimination of a methyl

$$\underset{\text{(A)}}{-C_2(=O_3)-O_1-\ddot{C}_4^-\,-} \longleftrightarrow \underset{\text{(B)}}{-C_2(-O_3^-)=O_1^+-\ddot{C}_4^-\,-}$$

proton are stabilized by an adjacent dipole[13] as in (B), and in general, the C_2-O_1 bond length is shorter in the carbanions than in the ground state as can be seen in Table 1.

Due to the n-σ^* interaction,[10] the anti form of the lone pair with respect to C_2-O_1 has longer bond length of C_2-O_1 compared with that in the syn form. Structural parameters for the anions formed in the product complexes are summarized

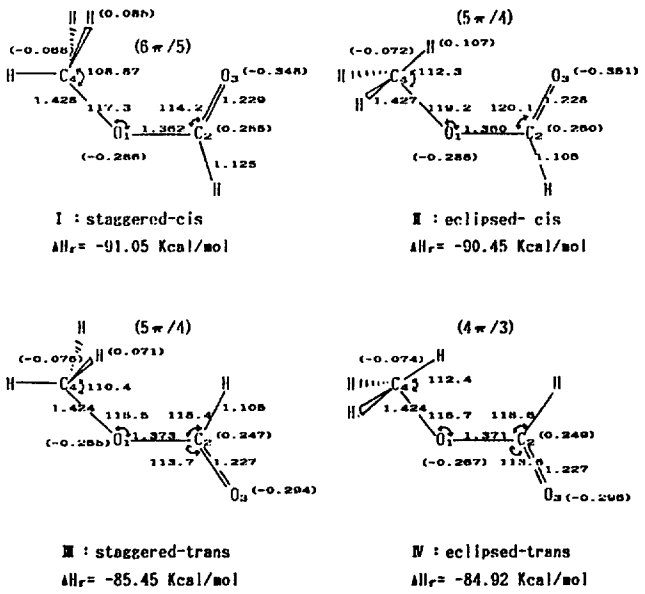

Figure 1. Structures, charges (in parentheses) and heats of formation of various conformers of methyl formate. ($n\pi/m$) denotes π-nonbonded structure with $n\pi$ electrons in m member nonbonded ring system.[10]

Table 1. Structual Parameter and Charges(q)

	ground state methyl formate	product complex			
		$^-NH_2$		^-OH	
		syn-form	anti-form	syn-form	anti-form
$d(O_1\text{-}C_2)$	1.362	1.349	1.357	1.346	1.354
$d(O_1\text{-}C_4)$	1.428	1.378	1.377	1.389	1.388
$d(C_2\text{-}O_2)$	1.229	1.242	1.244	1.241	1.243
$\angle O_1C_2O_3$	119.2	123.3	117.4	122.9	117.3
$\angle C_2O_1C_4$	117.3	121.7	117.5	121.2	117.3
$q(O_1)$	-0.286	-0.178	-0.146	-0.189	-0.159
$q(C_2)$	0.255	0.160	0.175	0.175	0.187
$q(O_3)$	-0.348	-0.457	-0.458	-0.449	-0.447
$q(C_4)$	-0.068	-0.569	-0.641	-0.528	-0.588

in Table 1.

Another consequence of the n-σ^* interaction is the stabilization of the anti form by 10 kcal/mol relative to the syn form. This AM1 result is in good agreement with a recent *ab initio* result on the relative carbanion stability showing that the anti form is favored by 6.0 kcal/mol.[13]

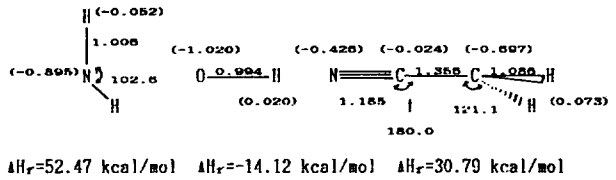

Figure 2. Structures and heats of formation of anions.

Table 2. Proton Affinities (PA) of Anions

	$^-NH_2$	^-OH	$^-CH_2CN$
Exp. value	403.7	390.8	327.1
AM1 value	403.7	391.0	377.9

The structures and heats of formation of the reactant anions are shown in Figure 2.

Proton affinity(PA) (basicity) of anion, B^-, is defined as[6k]

$$B^- + H^+ \rightarrow BH$$

$$PA(B^-) = \Delta H_f(H^+) + \Delta H_f(B^-) - \Delta H_f(BH) \quad (2)$$

The AM1 proton affinities calculated by eq.(2), for the three anions are presented in Table 2. Here we used the experimental $\Delta H_f(H^+)$ value of 367.2 kcal/mol instead of the unreasonably small AM1 $\Delta H_f(H^+)$ value of 314.9 kcal/mol.

Reference to Table 2 indicates that the calculated PAs as well as the relative order are remarkably in good agreement with those of the experimental values.

MO theoretical PAs reported in the literature show in general that they are not in satisfactory agreement with the experimental values unless very high level basis sets are used in the *ab initio* calculations.[14]

Reactivity. In the gas-phase ion-molecule reactions, the most exothermic reaction path is preferred.[15] Various reaction paths conceivable in the reactions of methyl formate with anions are summarized in Table 3 together with the enthalpies of reaction. The relative exothermicities are illustrated also in Figure 3. It can be seen that for all anion reactants studied, the reaction path in which $HC(=O)O^-$ is formed is the most exothermic, so that the $B_{AC}2'$ and S_N2 processes are the most favorable reaction modes considering the reaction enthalpies only. Recent experimental investigations on the gas phase reactions of methyl formate with vari-

Table 3. Reaction Modes and Heats of Reaction ($\Delta H_f°$)

Reaction	Mode of reaction	$\Delta H_f°$(kcal/mol)[a] $^-MH_2$	^-OH	$^-CH_2CN$
$^-XH + CH_3O\text{-}C(=O)H \rightarrow CH_3O\text{-}C(=O)^- + X_2H$	H_c^+-ABS[b]	-57.33	-42.70	-9.09
$\rightarrow CH_2O^-\text{--}HXH + CO$	CO-elim.	-24.24	-14.49	22.92
$\rightarrow CH_2O^- + XH_2 + CO$	CO-elim.	-12.88	1.75	35.36
$\rightarrow {}^-CH_2O\text{-}C(=O)H + XH_2$	H_m^+-ABS[c]	-27.86	-13.23	20.38
$\rightarrow CH_2O^- + HX\text{-}C(=O)H$	$B_{AC}2$[d]	-44.46	-30.71	12.74
$\rightarrow {}^-X\text{-}C(=O)H + CH_2OH$	$B_{AC}2'$[e]	-62.21	-61.30	-33.31
$\rightarrow HCO_2^- + HXCH_3$	S_N2	-78.24	-61.30	-36.16

[a] ΔH_f(prod.)-ΔH_f(react.). [b] formyl proton abstraction. [c] methyl proton abstraction. [d] carbonyl addition. [e] α-proton abstraction of attacking anions by the cleaving CH_3O^- ion in the $B_{AC}2$ path.

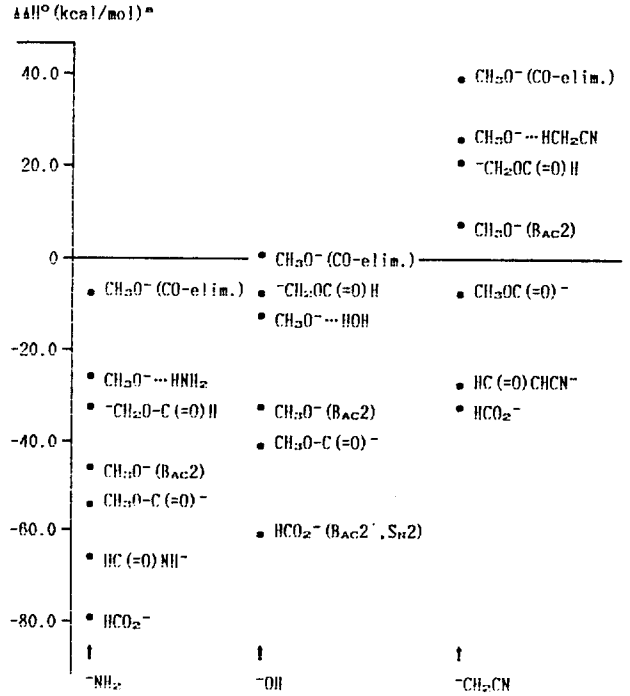

Figure 3. Heat of formation of product relative to the reactants ground state for reactions of methyl formate with anions. ª ΔH_f (prod.)-ΔH_f (react.).

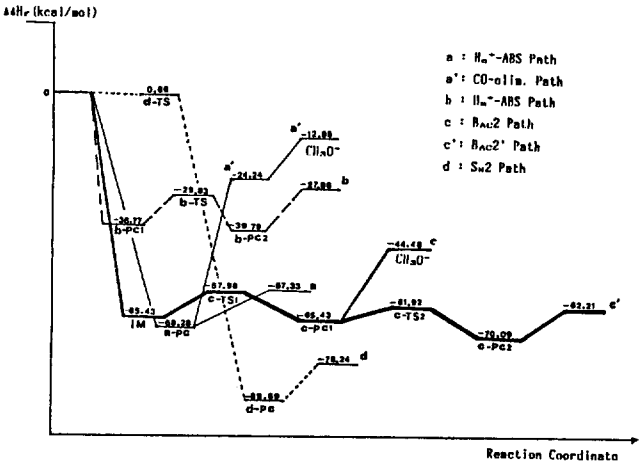

Figure 4. Potential energy profiles for the reaction of methyl formate with $^-NH_2$ (TS: Transition state, PC: Product complex, IM: Intermediate).

ous anions[5] have shown that the initial major products in the reaction with $^-NH_2$ corresponded to the proton abstraction path whereas the reactions with ^-OH and $^-CH_2CN$ gave the products from the $B_{AC}2'$ path. This indicates that the potential energy surface should plays an important role in understanding the reactivity of the reactions between methyl formate and anions. We have thus searched potential energy surfaces for all possible paths with each anions.

(1) Reaction with $^-NH_2$ Four reaction modes are allowed thermodynamically for the reaction of methyl formate with $^-NH_2$; proton abstractions (a and b), Carbonyl addition (c) and S_N2(d) processes. The potential energy profiles and stationary points structures are shown in Figure 4 and 5.

Proton abstractions are possible from either formyl H (a)

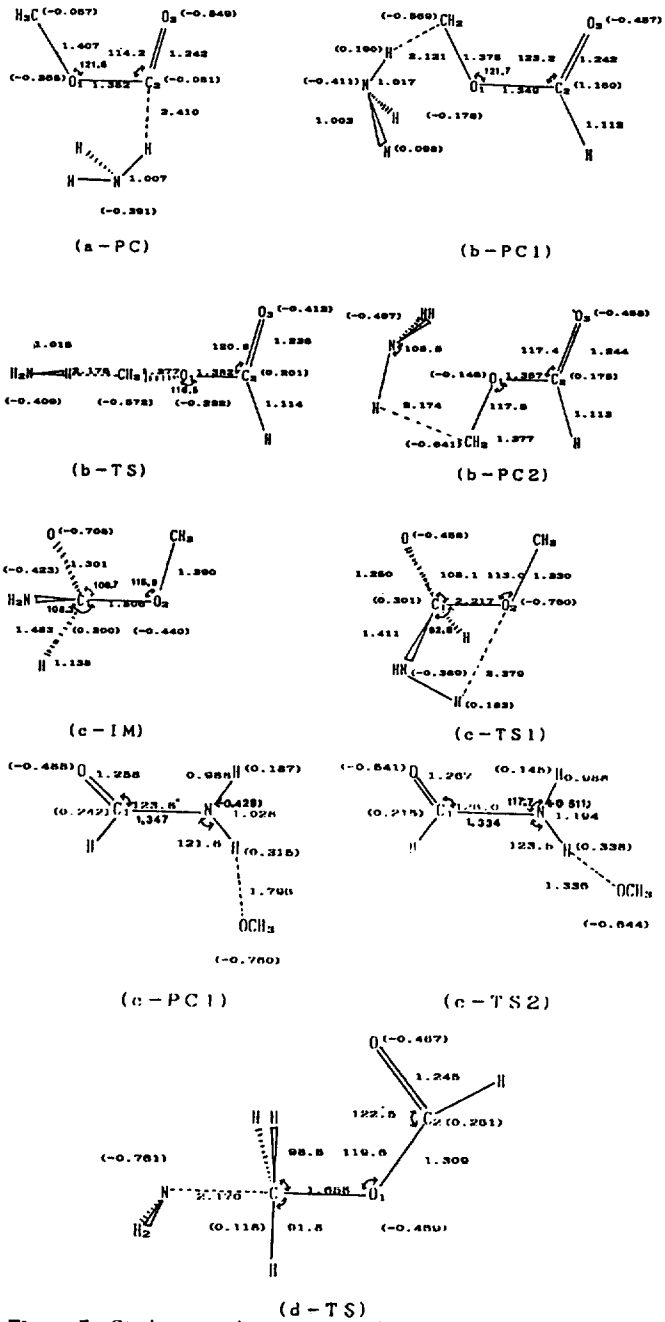

Figure 5. Stationary points structures in the reaction of methyl formate with $^-NH_2$.

attack on formyl H

Reactants → Product complex → Carbonyl anion (CH_3O-C(=O)$^-$) → CH_3O^- (CO elimin.)

Product complex → solvated anion (H_2N^----$HOCH_3$) (CO elimin.) → CH_3O^-

Scheme 1

or methyl H (b), the latter being more acidic as can be seen from the potential energy profiles in Figure 4. The product complex formed by the formyl proton abstraction proceeds to CO elimination as shown in Scheme 1. The CH_3O^- ion is produced from both the solvated anion and carbonyl anion but this anion can also be obtained from the $B_{AC}2$ path as can be seen in Figure 4. Experimentally, Riveros *et al.*[16] concluded that the proton abstraction path is the exclusive source of the CH_3O^- ion production. However, Johlman *et al.*[5a] have shown experimentally that both the proton abstraction and the $B_{AC}2$ paths are possible CH_3O^- production sources, as we found theoretically in this work. The CH_3O^- ion can not be formed directly from the attack on the formyl H but only through carbonyl anion or solvated anion (Scheme 1); this process is feasible when the carbonyl anion formed is very unstable or the solvated anion has enough thermal energy to break a weak hydrogen bond. This shows the importance of the stability of product complexes. The excess energy can be lost in various ways as shown in eq.(1).[17] If these energy dissipations were possible the reaction should proceed by the carbonyl anion formation because of its thermodynamic stability. However, in case the internal bond scission takes place in the product complex, prior to the energy loss, both the solvated anion and CH_3O^- productions are possible. The absolute product ratio should therefore largely depend on the reaction condition, but thermodynamically the formation of carbonyl anion is preferred to the formation of solvated anion and CH_3O^- ion.

In the reaction mode involving an attack on the carbonyl carbon (c), a tetrahedral intermediate (Figure 5) is formed in accordance with other theoretical studies.[18] The intermediate proceeds to form either CH_3O^- or $HC(=O)NH^-$ ion, many steps being involved in the latter path as can be seen in Figure 4. Recent *ab initio* MO theoretical studies by Yamabe *et al.*[19] and Jorgensen *et al.*[20] together with experimental solution chemistry indicated that the tetrahedral structure should be regarded as an intermediate when strong nucleophiles and poor leaving groups are involved, such as in the reaction studied in this work, while a tetrahedral TS is expected in opposite cases.

In the $B_{AC}2'$ path where the $HC(=O)NH^-$ ion is formed, the activation barrier of the TS1(*c*-TS1) is largely dependent upon the degree of bond breaking of the leaving group CH_3O^-. On the other hand, the barrier of the TS2(*c*-TS2) reflects the acidity of the substituted $^-NH_2$ anion.

Thus the carbonyl addition process(c) starts with a tight bond formation of the tetrahedral intermediate, which is followed by two paths leading to CH_3O^- ion and $HC(=O)NH^-$ ion production with the latter being favored by the thermodynamic stability.

The S_N2 process(d) leads to very stable products, but no reactant complex formation prior to the TS was observed (Figure 4). This is because a methyl proton abstraction occurs as the reactant anion $^-NH_2$ approaches to the methyl carbon atom. However when the anion approaches nearer to the methyl carbon instead of the methyl hydrogens, the S_N2 TS(*d*-TS) shown in Figure 5 was obtained. There were two negative eigenvalues in the force constant matrix (−1.83702 and −0.00048), but the normal vector analyses showed that the very small negative eigenvalue was not of the stretching mode of the reaction coordinate bond but cooresponded to the bending modes of the methyl and amide hydrogens. This means that the TS shown in Figure 5 is the correct S_N2 TS. The S_N2 barrier in Figure 3 due to this TS (*d*-TS) is very high indeed relative to other barriers so that unless the reactants have enough energies at the initial stage of the reaction the S_N2 process should hardly compete with other processes.

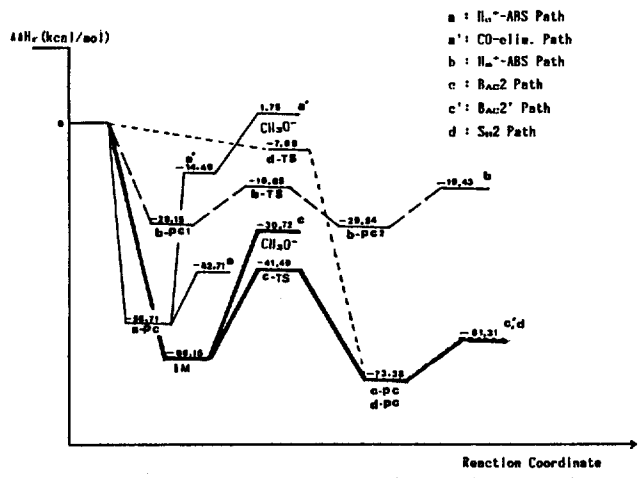

Figure 6. Potential energy profiles for the reaction of methyl formate with ^-OH (TS: Transition state, PC: Product complex, IM: Intermediate).

Table 4. Semiempirical and *ab initio*[a] Solvation Energies

	AM1	MNDO	3-21G	4-31G	6-31G[a]//4-31G
NH_3	−11.36	−11.04			
H_2O	−16.24	−7.34	−37.19	−30.47	−24.37
CH_2CN	−12.44	−8.90			

[a] In hartrees; otherwise in kcal/mol.

On the whole, the carbonyl anion and $HC(=O)NH^-$ ion formation paths are thermodynamically favored in the reaction of methyl formate with $-NH_2$, but the product stabilities in the two path are comparable and relatively complex steps are involved in the $HC(=O)NH^-$ ion path so that the carbonyl anion path may be preferred. Moreover, the product in the methyl proton abstraction $^-CH_2OC(=O)H$, has the same mass ($m/e = 59$) as the carbonyl anion, $CH_3OC(=O)^-$, and may result in an apparent increase of the proton abstraction process.

(2) Reaction with ^-OH. The same four modes (a - d) of reactions are also possible with ^-OH: proton abstractions (a and b), carbonyl addition (c), and S_N2(d) processes. Since ^-OH has somewhat lower proton affinity than $^-NH_2$, the proton abstraction processes of ^-OH are relatively less favorable compared to those of $^-NH_2$ as can be seen from Figure 6. In the formyl proton abstraction, the product complex leads to the carbonyl anion and the solvated anion formation as we found in the corresponding reaction of $^-NH_2$. The AM1 and MNDO solvation energies obtained in this work are summerrized in Table 4 together with those by the ab initro calculations. Comparison of the values in Table 4 indicates that the AM1 method is relatively better than MNDO, and the 3-21G results[21] overestimate the solvation energy when compared with the calculations at the 6-31G*//4-13G leval.[22] It is interesting to note that the AM1 results are closer to those at the

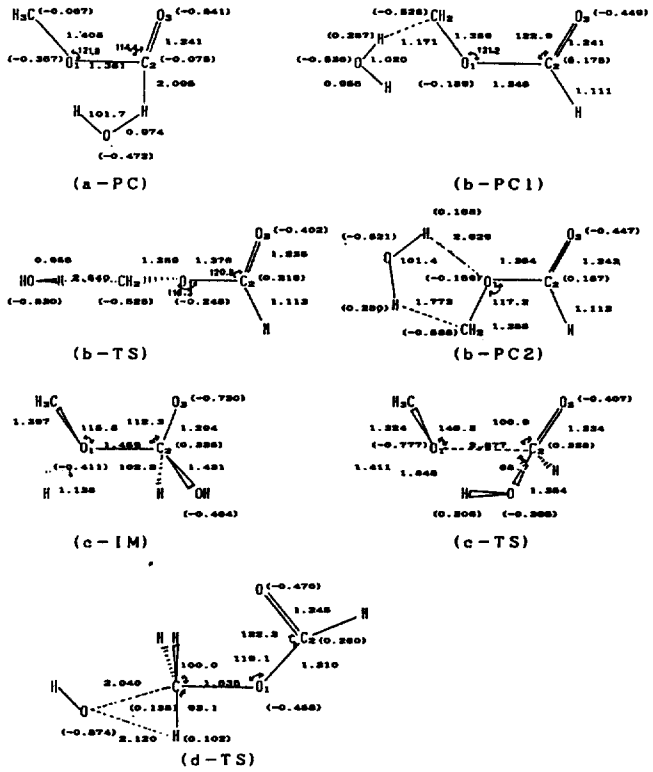

Figure 7. Stationary points structures in the reaction of methyl formate with $^-$OH.

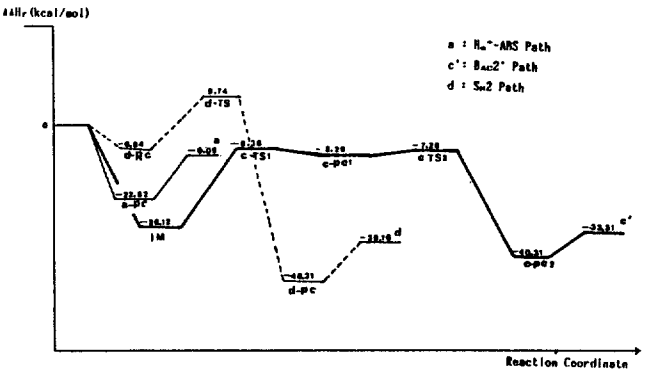

Figure 8. Potential energy profiles for the reaction of methyl formate with $^-CH_2CN$ (TS: Transition state, PC: Product complex, IM: Intermediate).

6-31G*//4-31G level than the lower level *ab initio* results using 3-21G basis set.

The potential energy profiles and the stationary points structures are presented in Figures 6 and 7. The CH_3O^- ion formation after the formyl proton abstraction is shown to be an endothermic process in Figure 6 in contrast to the exothermic (-3.7 kcal/mol) nature of the process experimentally. However even this exothermicity is unfavorable compared to the CH_3O^- ion formation in the $B_{AC}2$ process. Again with $^-$OH, the solvated ion and carbonyl ion ($CH_3OC(=O)^-$) formations are possible after the formyl proton abstraction as they were with $^-NH_2$. Here also the mode of excess energy dissipation of the product complex will affect the ratio of the ions produced. The carbonyl anion formation is thermodynamically more favored than the solvated anion formation so that the carbonyl anion formation will be more facile.

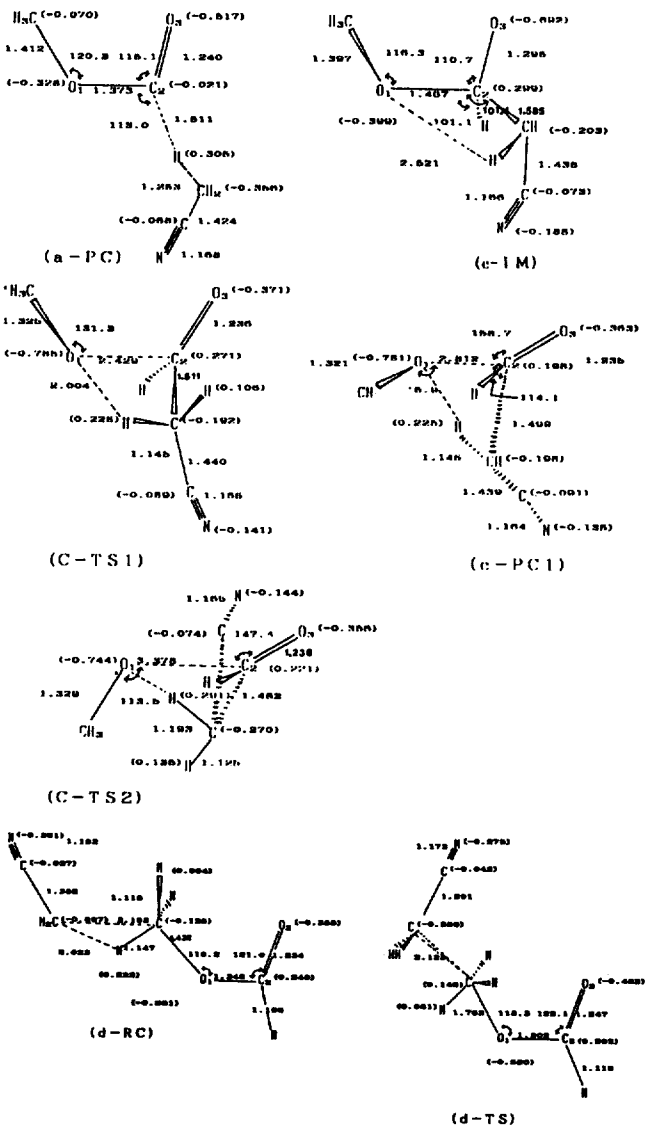

Figure 9. Stationary points structures in the reaction of methyl formate with $^-CH_2CN$.

In the carbonyl addition process, a tetrahedral intermediate is formed in the first step and subsequent CH_3O^- and HCO_2^- ion formations ($B_{AC}2'$) follow, as can be seen Figures 6 and 7. HCO_2^- ion formation is thermodynamically favored relative to the CH_3O^- formation. The barrier height in the $B_{AC}2'$ path reflects both the nucleophilicity of the $^-$OH ion and the acidity of the substituted $^-$OH; thus the nucleophilicity of $^-$OH appears to be weaker than that of $^-NH_2$ qualitatively judging by the barrier heights, while the acidity of $^-$OH seems to be greater since no barrier exists in the case of $^-$OH reaction.

In the S_N2 process there is no reactant complex but a TS is obtained as shown in Figures 6 and 7. The HCO_2^- ion formation should result solely through the $B_{AC}2'$ process, since the S_N2 TS constitutes a high energy barrier in the overall potential energy profile.

On the whole, in the reaction with $^-$OH the proton abstraction process is less favorable than in the reaction with $^-NH_2$ due to somewhat weaker proton affinity. However the $B_{AC}2'$ process is greatly favored compared with the formyl proton

abstraction thermodynamically. The activation barrier in the $B_{AC}2'$ process is comparable to the energy for the product formation in the formyl proton abstraction process. These trends indicate that the $B_{AC}2'$ processis is favored over the proton abstraction in the reaction of methyl formate with $^-NH_2$.

(iii) Reaction with $^-CH_2CN$ ion. The $^-CH_2CN$ ion has considerably weaker proton affinity compared to the $^-NH_2$ and ^-OH ions, making the proton abstraction process more difficult accordingly. The methyl proton abstraction path is not allowed thermodynamically (Table 3) and in the formyl proton abstraction the solvated anion formation is not possible from the product complex as can be seen in Figure 8 and 9 in contrast to the reactions with $^-NH_2$ and ^-OH.

The carbonyl addition process proceeds through an intermediate formation producing $HC(=O)CHCN^-$ ion ($B_{AC}2'$ process), since the $B_{AC}2$ process is unfavorable thermodynamically (Figures 8 and 9). The activation barrier in the $B_{AC}2'$ path (*c*-TS1) is a measure of the nucleophilicity of the $^-CH_2CN$ ion and the barrier height of the TS2(*c*-TS2) reflects the acidity of the $^-CH_2CN$ ion. The barrier height of the TS1 (*c*-TS1) is higher than the corresponding barrier height for the $^-NH_2$ ion, while that of the TS2 (*c*-TS2) is lower than that for the $^-NH_2$ ion; this indicates that the nucleophilicity is weaker while the acidity is stronger for $^-CH_2CN$ than for the $^-NH_2$. The acidity of the substituted anions is in the order of $^-OH > ^-CH_2CN > ^-NH_2$.

In the S_N2 process, a reactant complex is formed between the methyl proton and the $^-CH_2CN$ anion, since proton abstraction is impossible. The S_N2 TS has a positive (endothermic) barrier height so that the S_N2 process should be forbidden thermodynamically.

On the whole, the $B_{AC}2'$ process is favored compared to the formyl proton abstraction. Since the methyl proton abstraction is impossible, the $B_{AC}2'$ process will be more facile than the corresponding process in the reaction with ^-OH.

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