Theoretical Study of the aza-Wittig Reactions of $X_3P{=}NH$ (X=H and Cl) with Formaldehyde in Gas Phase and in Solution

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Received: February 20, 2002; In Final Form: June 28, 2002

The aza-Wittig reaction of iminophosphoranes ($X_3P{=}NH$, X=H and Cl) with formaldehyde (H_2CO) was investigated in gas phase and in water using ab initio MP2/6-31G** level of theory and the self-consistent reaction field theory (isodensity polarized continuum model, IPCM). In the gas phase, the aza-Wittig reaction was predicted to be a two-step process with two dipole−dipole complexes, one four-membered ring intermediate and two transition states. The potential energy profiles along the minima energy path in gas phase and in water were obtained. The solvent effects on the thermodynamic and kinetic properties of this reaction were discussed. This aza-Wittig reaction is more favorable for X=H than for X=Cl, both in the gas phase and in water.

1. Introduction

Iminophosphoranes have attracted much attention due to their wide application to organic synthesis since they were first prepared in 1919 by Staudinger and Meyer.[1] As the isoelectronic compounds with the Wittig reagent methylenephosphoranes, iminophosphoranes were proved to have versatile properties and to undergo a series of interesting chemical reactions.[2−7] The aza-Wittig reaction of iminophosphoranes with carbonyl compounds is one of the important reactions because such a reaction is an excellent method by which to introduce a C=N double bond. In the literature, a few theoretical studies on the structural and electronic properties of iminophosphoranes and the mechanism of the aza-Wittig reaction have appeared,[8−11] Koketsu et al.[9] reported the results of ab initio calculations at the MP2/D2-d level on the mechanism and energetics of the reaction of iminophosphanes (H_3MNH, M=P, As, Sb, and Bi) with formaldehyde (H_2CO). They found that this aza-Wittig reaction is a two-step process for any M, and that the four-membered ring intermediate between two transition states is not only one. In the other words, the first transition state TS1 connects the reactant complex RC and intermediate 1 (INT1), while second transition state TS2 connects the product complex PC and intermediate 2 (INT2). INT2 is about 2−5 kcal/mol less stable than INT1 and has a pseudorotational transition state at the M center. Lu et al.[11] studied the aza-Wittig reaction of $X_3P{=}NH$ (X=Cl, H, and CH_3) with O=CHCOOH using the MP2/6-31G** method at the HF/6-31G** optimized structures. They obtained two similar intermediates for X=H and Cl (for X=CH_3, there is only one intermediate) at the HF/6-31G** level and proved that these two intermediates became accurately one minimum when the MP2/6-31G** method was used in the structure optimization.

In the present study, we have performed ab initio calculations at the MP2/6-31G** level of theory for the title aza-Wittig reactions of $X_3P{=}NH$ with H_2CO (X=H and Cl) (Scheme 1) in order to examine the identity of INT1 and INT2 and to get more detailed information about these reactions in gas phase. The other goal of this work is to investigate the solvent effects on the thermodynamic and kinetic properties of the aza-Wittig reaction. It is well known that solvent effects play an important role in determining transition states, rates of reaction, equilibrium constants, and the other quantities of chemical and biochemical processes. The reaction in solution is probably different from that in gas phase, especially for a stepwise process. In other words, in solution the step with the highest reaction barrier will be the rate-determining step because excess energy from the reaction system will disperse to solvent molecules. In the literature there were not any experimental and theoretical studies on the title aza-Wittig reaction in solution. Our present work may provide some theoretical information about solvent effects on this reaction. In this study, the potential energy profiles of the ($X_3P{=}NH + H_2CO$) reaction system in gas phase and in water were obtained by using the ab initio MP2/6-31G** method and the self-consistent reaction field theory (isodensity polarized continuum model, IPCM).

2. Computational Details

Ab initio molecular orbital calculations were carried out using the Gaussian 98 program.[12] The structures of all the reactant complexes, product complexes, intermediates, and transition states were optimized at the second-order Møller−Plesset perturbation level with the 6-31G** basis set (MP2/6-31G**). The nature of the stationary point was confirmed by the harmonic frequency analysis as a minimum with all positive frequencies or as a transition state with only imaginary frequencies. Three minima (reactant complex (RC), intermediate (INT), and product complex (PC)) and two transition states (TS1 and TS2) were obtained. The frequency calculations at the MP2/6-31G** level without scaling also provided the thermodynamic quantities such as the zero-point vibrational energy, thermal correction, enthalpies, Gibbs free energies, and entropies at temperature of 298.15 K and pressure of 1 atm.

The intrinsic reaction coordinate (IRC) calculations[13] were performed to realize the connections between RC and INT through TS1 as well as between INT and PC through TS2. At the same time, IRC performance with the "IRC=tight" option was used to generate the minimum energy path (MEP) in gas phase for the $X_3P{=}NH + H_2CO$ reaction systems (X=H and

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10.1021/jp020466z CCC: $22.00

SCHEME 1

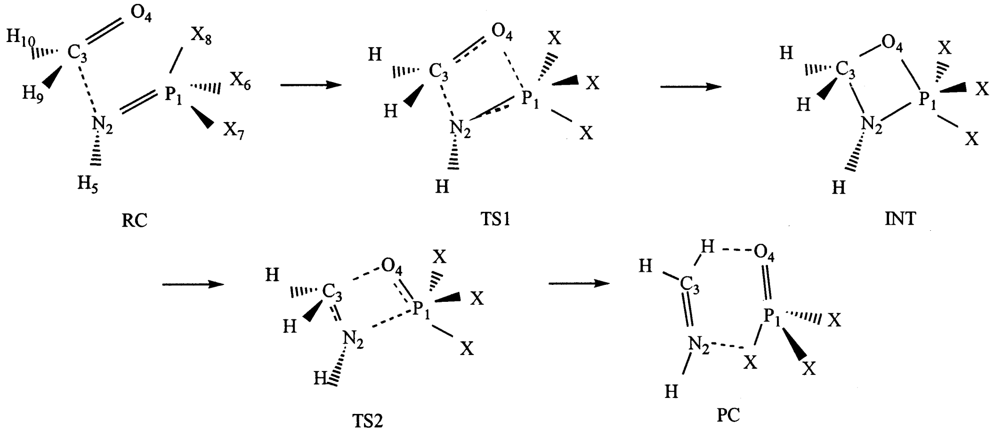

TABLE 1: Selected Geometric Parameters Optimized at the MP2/6-31G Level of Theory for the aza-Wittig Reaction**[a]

X		RE[b]	RC	TS1	INT	TS2	PC
H	r (P_1N_2)	1.572	1.577	1.609	1.689	2.244	3.034
	r (N_2C_3)		2.674	1.963	1.463	1.335	1.284
	r (C_3O_4)	1.220	1.224	1.258	1.410	1.834	3.105
	r (P_1O_4)		3.359	2.434	1.787	1.572	1.502
	r (P_1X_8)	1.389	1.388	1.390	1.397	1.389	1.397
	$\alpha(P_1N_2C_3)$		104.1	98.8	95.5	83.8	103.0
	$\alpha(N_2C_3O_4)$		103.4	99.1	95.2	101.3	81.3
	$\alpha(H_5N_2P_1)$	115.6	115.9	114.9	127.2	105.9	147.0
	$\tau(P_1N_2C_3O_4)$		0.0	0.0	−7.9	12.3	0.0
	$\tau(H_5N_2C_3P_1)$		180.0	−179.9	−146.9	−104.7	180.0
Cl	r (P_1N_2)	1.535	1.541	1.595	1.653	2.020	3.238
	r (N_2C_3)		2.943	1.966	1.453	1.318	1.282
	r (C_3O_4)	1.220	1.221	1.259	1.426	1.997	3.132
	r (P_1O_4)		3.675	2.342	1.725	1.554	1.478
	r (P_1X_8)	1.998	1.994	2.012	2.040	2.040	2.007
	$\alpha(P_1N_2C_3)$		103.4	97.1	95.7	93.4	106.3
	$\alpha(N_2C_3O_4)$		105.2	95.6	93.8	89.7	76.8
	$\alpha(H_5N_2P_1)$	120.0	118.2	113.1	132.0	112.8	143.8
	$\tau(P_1N_2C_3O_4)$		23.3	−15.6	0.1	17.6	0.0
	$\tau(H_5N_2C_3P_1)$		−130.6	−160.4	179.7	−116.7	−179.8

[a] Bond lengths in Å, bond angles in degrees; [b] Separated reactants.

Cl). The MEPs at the MP2/6-31G** level were constructed with a step size of 0.05 amu$^{1/2}$ bohr in both directions from the TS1 and with a step size of 0.10 amu$^{1/2}$ bohr in both directions from the TS2. To consider the solvent effect on the aza-Wittig reaction, the isodensity polarized continuum model (IPCM)[14] was applied. Single-point energy calculations were done at the MP2/IPCM/6-31G** level using the geometries along the minimum energy path. As a result, we have obtained two potential energy surfaces for X=H and Cl in the gas phase as well as in the aqueous solution. The free energy changes in solution were computed by using the electronic energy changes derived from IPCM calculation and the entropy changes in gas phase.

3. Results and Discussions

3.1. Gas-Phase Reactions. *3.1.1. Geometries.* We have determined the structures of $X_3P{=}NH + H_2CO$ reaction systems for X=H and Cl at MP2/6-31G** level and found there are the three minima RC, INT, and PC, and two transition states, TS1 and TS2, on the potential energy surface. The selected optimized geometrical data of all stationary points along the reaction path are listed in Table 1 along with the geometric parameters of isolated reactants $X_3P{=}NH$ (X=H and Cl) and H_2CO. Figure 1 depicts the optimized structures of RC, TS1, INT, TS2, and PC of iminophosphorane for X=H. As shown in Table 1, the geometries of the components of the resultant reactant complex show very little distortion from their monomer geometries. For X=H, RC has a planar structure and H_5 is in the plane of PNCO. For X=Cl, however, RC shows a nonplanar structure with dihedral angle (PNCO) of 23.3°. All of the predicted product complexes are planar in the PNCO ring for X=H and Cl. There is the distinct difference to the molecular geometry of the first transition state TS1, in which the dihedral angles (PNCO) are 0.0 and −15.6°, respectively. For the second transition state TS2, the dihedral angle PNCO (12.3°) for X=H is also different from that of X=Cl (17.6°). It is noted that there is only one intermediate between TS1 and TS2 at the MP2/6-31G** level of theory. This is different from the previous research reported by Kiketsu et al.[9] for the reactions of iminophosphoranes ($H_3M{=}NH$, M=P, As, Sb, and Bi) with H_2CO at the MP2/DZ-d level, where one intermediate and one pseudorotational transition state at the M atom between TS1 and TS2 were found. In the present study, IRC calculations for X=H and Cl confirm that TS1 connects RC and INT, while TS2 connects INT and PC, as shown in Figure 1. This only intermediate is a stable four-membered ring molecule. Thus, the title aza-Wittig reaction is shown to proceed: the first step is attacking of carbon and oxygen atoms in formaldehyde to nitrogen and phosphorus in iminophosphorane, respectively, to form a four-membered cyclic intermediate via TS1, and the second step corresponds to the cycloreversion of the intermediate to yield $H_2C{=}NH$ and the phosphorus oxides $X_3P{=}O$ (X=H and Cl).

3.1.2. Energetics. The MP2/6-31G** predicted total relative energies to separated reactants are given in Table 2 for the aza-Wittig reaction. One can see from Table 2 that the reactant complex (RC) is more stable than the separated reactants by 6.318 and 3.296 kcal/mol for X=H and Cl, respectively. However, the Gibbs free energy changes from the separated reactants to RC are calculated to be −0.251 and 4.759 kcal/mol for X=H and Cl. For X=Cl, the positive free energy change indicates that the formation of the reactant complex may be an unspontaneous process. For the first step of the aza-Wittig reaction, from RC to INT, the activation energy barrier increases in the order H (10.56) < Cl (22.60 kcal/mol). The activation barrier of the second step agrees with this order, H (20.95) < Cl (32.38 kcal/mol). Because the energy in TS1 is much higher than that in TS2 (see Table 2), the overall activation barrier should correspond to the difference in energy between the separated reactants $X_3P{=}NH + H_2CO$ and TS1, being 4.24 and 19.30 kcal/mol for X=H and Cl, respectively. Therefore, the

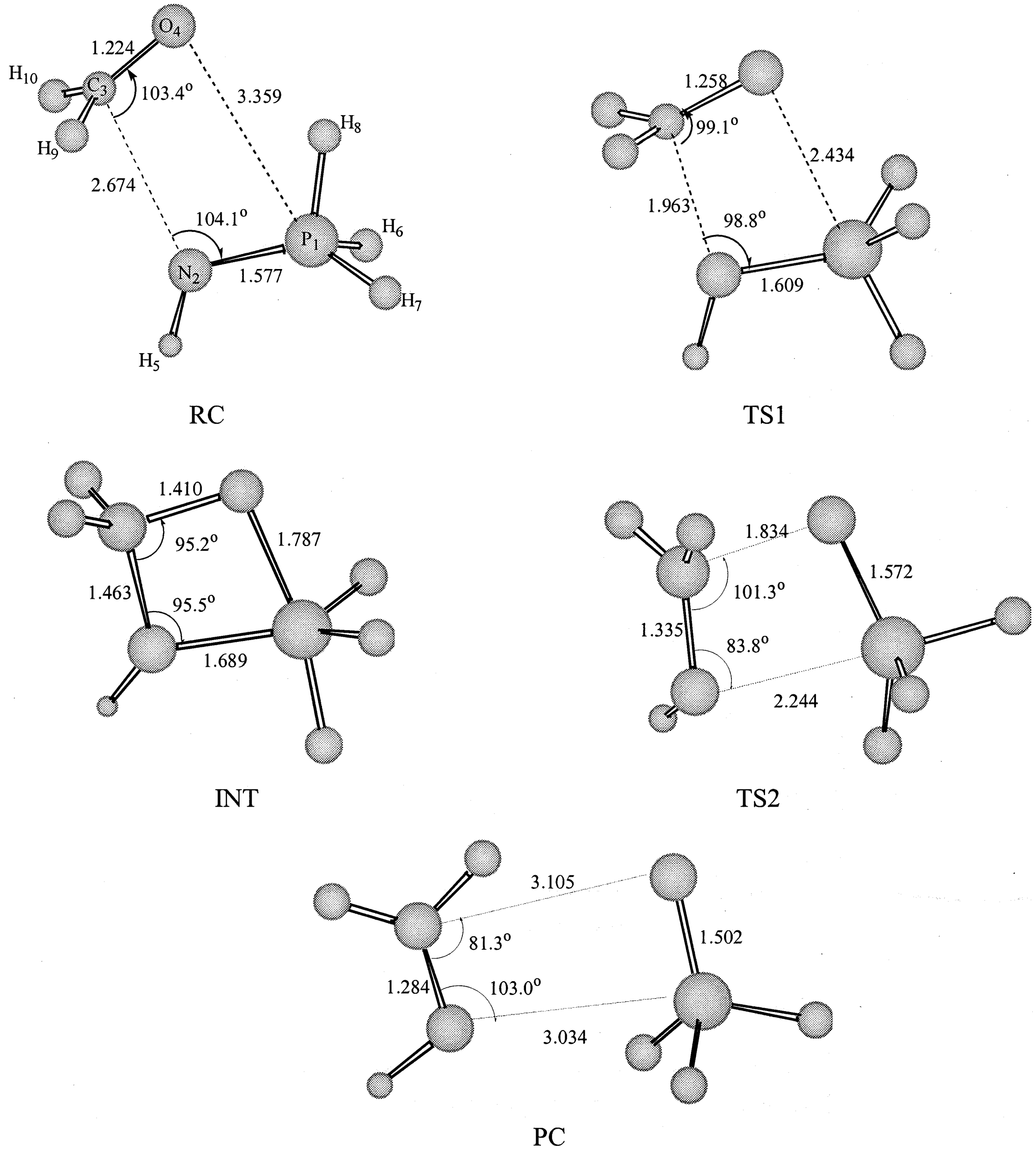

Figure 1. Optimized structures of reactant and product complexes (RC and PC), intermediate (INT), and transition states (TS1 and TS2) at the MP2/6-31G** level of theory for the aza-Wittig reaction of $X_3P{=}NH$ and $H_2C{=}O$ (X=H and Cl) (bond length in Å).

TABLE 2: Relative Total Energies in Gas Phase (kcal/mol)

X		ΔE	ΔE_{ZPV}	ΔH	ΔG
H	RE	0.000	0.000	0.000	0.000
	RC	−6.318	−4.874	−4.770	−0.251
	TS1	4.242	6.689	5.858	12.791
	INT	−25.087	−19.395	−20.871	−12.235
	TS2	−4.142	0.364	−1.162	7.467
	PC	−33.490	−30.257	−30.395	−25.292
Cl	RE	0.000	0.000	0.000	0.000
	RC	−3.296	−2.484	−2.557	4.759
	TS1	19.303	21.718	20.216	31.999
	INT	−24.339	−19.109	−20.863	−8.757
	TS2	8.042	11.923	10.034	23.023
	PC	−30.540	−27.763	−28.257	−19.391

aza-Wittig reaction $X_3P{=}NH + H_2CO$ may be much more favorable for X=H than for X=Cl.

The thermodynamical data for two elementary steps of aza-Wittig reactions were calculated using MP2/6-31G** method at temperature of 298.15 K and 1 atm and are shown in Table 3. It is found that the first and the second steps for X=H and Cl are all exothermic processes. However, the more exothermic reaction in the first step (X=Cl) has a higher activation barrier in comparison with that for X=H. The comparable values for the overall enthalpy variation ΔH°_{tot} are predicted to be −25.625 and −25.700 kcal/mol for X=H and Cl, respectively. This is inconsistent with Hammond's postulate.[15] This was also observed in the research to the reactions of $X_3P{=}NH$ with $O{=}CHCOOH$ (X=Cl, H, and CH_3) reported by Lu et al.[11] Such an unusual correlation may be ascribed to the following factors. The previous theoretical investigation has shown that although the Wittig reaction is formally a symmetry-forbidden (2s+2s) addition, polar characters of the reagents make the reaction rather easy.[16] As for the isoelectronic compounds of methylenephosphogens, the increasing polarization of iminophosphoranes should also be responsible for the destabilization of reactants. So the stronger polarity of $H_3P{=}NH$ with the dipole moment of 3.555 D compared to $Cl_3P{=}NH$ (1.436 D) means that the exchange of =NH in $X_3P{=}NH$ and =O in $H_2C{=}O$ is easier for X=H than for X=Cl. The Mulliken charges of relevant

TABLE 3: Changes of Electronic Energies, Zero Point Vibration Energies, Enthalpies, and Entropies for All Steps in the aza-Wittig Reactions of $X_3P{=}NH + H_2C{=}O$ (X=H and Cl) (at 298.15 K and 1 atm)[a]

X		step 1[b]			step 2[b]			
		$\Delta^{\ddagger}$	$\Delta^{\ddagger}_{-1}$	Δ°	$\Delta^{\ddagger}$	$\Delta^{\ddagger}_{-1}$	Δ°	$\Delta^{\circ}_{\text{total}}$
H	ΔE	10.560	29.329	−18.769	20.945	29.348	−8.403	−27.172
	ΔE_{ZPV}	11.563	26.084	−14.521	19.759	30.621	−10.862	−25.383
	ΔH	10.628	26.729	−16.101	19.709	29.233	−9.524	−25.625
	ΔS	−8.095	5.714	−13.809	0.027	−11.822	11.849	−1.960
Cl	ΔE	22.599	43.642	−21.043	32.381	38.582	−6.201	−27.244
	ΔE_{ZPV}	24.202	40.827	−16.625	31.032	39.686	−8.654	−25.279
	ΔH	22.773	41.079	−18.306	30.897	38.291	−7.394	−25.700
	ΔS	−14.981	1.085	−16.066	−2.969	−13.834	10.865	−5.201

[a] ΔE, ΔE_{ZPV}, and ΔH are in kcal/mol, ΔS in cal/(mol.K). [b] $\Delta^{\ddagger}$, $\Delta^{\ddagger}_{-1}$, and Δ° denote the forward barrier of activation, the backward barrier of activation, and the barrier of reaction in one elemental step, respectively.

TABLE 4: Charges of Reactant Complex and Changes in Charges, $\Delta q^{\ddagger}$ and Δq° Involved in Step 1 of the aza-Wittig Reaction of $X_3P{=}NH + H_2C{=}O$ (X=H and Cl) at the MP2/6-31G Level of Theory (in electronic charge unit)[a]**

X		P_1	N_2	C_3	O_4
H	$q^{(RC)}$	0.876	−0.902	0.319	−0.534
	$\Delta q^{\ddagger}$	0.101	−0.049	0.089	−0.184
	Δq°	0.213	0.116	0.001	−0.256
Cl	$q^{(RC)}$	0.901	−0.773	0.284	−0.491
	$\Delta q^{\ddagger}$	0.111	−0.105	0.121	−0.210
	Δq°	0.247	0.021	0.018	−0.238

[a] $\Delta q^{\ddagger} = q^{(TS1)} - q^{(RC)}$, $\Delta q^{\circ} = q^{(INT)} - q^{(RC)}$.

TABLE 5: Percentage of Evolution of Bond Order (%*Ev*) and Synchronicity (*Sy*) along Step 1 and Step 2 of the aza-Wittig Reaction for $X_3P{=}NH + H_2C{=}O$ (X=H and Cl) at the MP2/6-31G Level of Theory**

X	%*Ev*				Sy
	P_1N_2	N_2C_3	C_3O_4	P_1O_4	
			RC → TS1 → INT		
H	32.47	17.43	23.19	11.10	0.785
Cl	52.87	17.51	24.03	12.66	0.675
			INT → TS2 → PC		
H	85.24	65.21	75.93	66.06	0.932
Cl	70.94	73.97	85.38	60.11	0.935

atoms and their changes from reactant complex to transition state TS1 and to intermediate for X=H and Cl are shown in Table 4. The reactant complex has a positive charge on the P_1 atom and a negative charge on the N_2 atom for the two compounds. In TS1, the charge on P_1 becomes more positive. The increase in positive charge of the P_1 atom implies that the rate will decrease when more electron withdrawing Cl atoms are as substituents on the P_1 atom. Therefore, the reaction activation barrier for X=H may be expected to be much lower than that for X=Cl, even though the reaction energies are comparable for X=H and Cl.

3.1.3. Bond Order Analysis. To gain insight into the various bond-breaking or bond-making processes, an analysis of bond order is carried out. The bond order (*B*) can be defined according to the Pauling expression:[17]

$$B_i^{\text{SP}} = \exp\left(\frac{r_i(1) - r_i(\text{SP})}{0.3}\right) \tag{1}$$

where $r_i(\text{SP})$ is the length of bond *i* at the stationary point (SP) and $r_i(1)$ is the reference bond length. The percentage of evolution of bond orders (%*Ev*) is given by

$$\%Ev = \frac{B_i^{\text{TS}} - B_i^{\text{RE}}}{B_i^{\text{PR}} - B_i^{\text{RE}}} \times 100 \tag{2}$$

where the superscripts TS, RE, and PR refer to the transition state, reactant, and product, respectively. Substituting the Pauling bond order expression (1) for the B_i in eq 2, %*Ev* becomes

$$\%Ev = \frac{\exp(-r_i^{\text{TS}}/0.3) - \exp(-r_i^{\text{RE}}/0.3)}{\exp(-r_i^{\text{PR}}/0.3) - \exp(-r_i^{\text{RE}}/0.3)} \times 100 \tag{3}$$

Another concept, synchronicity (*Sy*), proposed by Moyano et al.[18] is used to represent the global nature of bond breaking/forming processes in the decomposition reaction and expressed by

$$Sy = 1 - \frac{\displaystyle\sum_{i=1}^{n} \frac{|(\%Ev)_i - (\%Ev)_{\text{av}}|}{(\%Ev)_{\text{av}}}}{2n - 2} \tag{4}$$

In eq 4, *n* denotes the number of bonds directly involved in the reaction, and the average $(\%Ev)_{\text{av}}$ is therefore

$$(\%Ev)_{\text{av}} = n^{-1} \sum_{i=1}^{n} (\%Ev)_i \tag{5}$$

The related bond lengths, percentage of evolution of bond orders (%*Ev*), and synchronicity (*Sy*) are presented in Table 5. From Table 5, for step 1 of the aza-Wittig reaction of $X_3P{=}NH + H_2CO$, the %*Ev* values of TS1 are similar and very small for X=H and Cl, and indicate that the structures of TS1 are very early and reactant-like. The $P_1{-}N_2$ and $C_3{-}O_4$ bond-changing from double bond to single bond is more advanced than $N_2{-}C_3$ and $P_1{-}O_4$ bond-forming process. The synchronicity values of 0.785 and 0.675 for X=H and Cl, respectively, show that the first step of this reaction is asynchronous concerted process.

For the four-membered ring intermediate opening, step 2 of the aza-Wittig reaction, the %*Ev* values (see Table 5) indicate that the $P_1{-}N_2$ and $C_3{-}O_4$ bond-breaking is more advanced than the $N_2{-}C_3$ and $P_1{-}O_4$ bond-changing from single bond to double bond for X=H and Cl. In the cleavage process of $P_1{-}N_2$ and $C_3{-}O_4$ bonds, the $P_1{-}N_2$ bond-breaking is slightly more advanced than the $C_3{-}O_4$ bond-breaking for X=H, which is different from the case in X=Cl where the $P_1{-}N_2$ bond-breaking is later. For the bond-changing from single bond to double bond, while $N_2{-}C_3$ bond-changing is more advanced than that of the $P_1{-}O_4$ bond for X=Cl, the trend is almost same for X=H. The synchronicity values of 0.932 and 0.935 for X=H

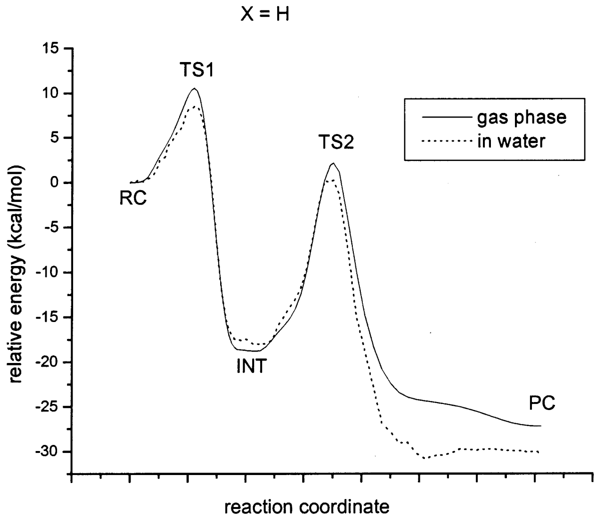

Figure 2. Minimum energy path E_{MEP}(s) for the aza-Wittig reaction of $H_3P{=}NH$ with $H_2C{=}O$ in gas phase and in water.

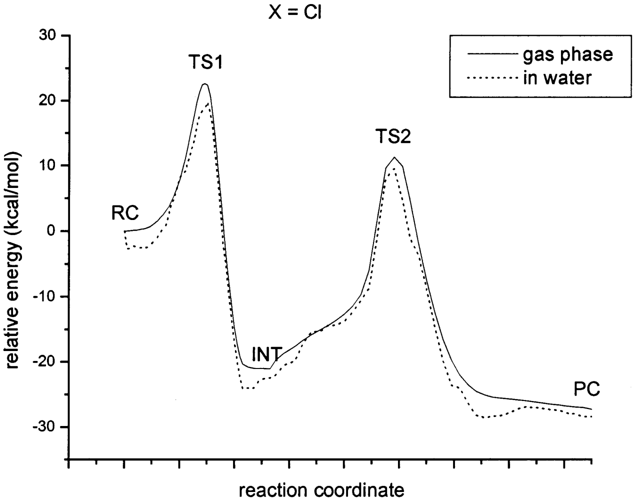

Figure 3. Minimum energy path E_{MEP}(s) for the aza-Wittig reaction of $Cl_3P{=}NH$ with $H_2C{=}O$ in gas phase and in water.

and Cl reveal that the cycloreversion of the cyclic intermediate can be viewed as very synchronous process.

3.2. Solvent Effects Calculated via Reaction Field Theory. According to the IRC theory, the minimum energy path (MEP) in gas phase was calculated at the MP2/6-31G** level with the step sizes of 0.05 and 0.10 $(amu)^{1/2}$ bohr for step 1 and step 2 of the aza-Wittig reaction $X_3P{=}NH + H_2CO$ (X=H and Cl). Figures 2 and 3 depict the relative potential energy profiles V_{MEP}(s) along the MEP in gas phase for X=H and Cl, respectively. For all of the structures in the MEP, the single-point energies in water were calculated using the isodensity polarized continuum model (IPCM). The dielectric constant ϵ was assumed to be 78.3 for the bulk water. As a result, two potential energy curves for the aza-Wittig reactions (X=H and Cl) in the aqueous solution were also obtained and are shown in Figures 2 and 3, respectively. The free energy changes of activation and reaction of step 1 and step 2 are listed in Table 6.

TABLE 6: Free Energy Changes in Gas Phase and Solution (kcal/mol)

	in gas phase				in water			
X	$\Delta G_1^\ddagger$	$\Delta G_2^\ddagger$	ΔG_1°	ΔG_2°	$\Delta G_1^\ddagger$	$\Delta G_2^\ddagger$	ΔG_1°	ΔG_2°
H	13.04	19.70	−11.98	−13.06	10.94	18.27	−13.94	−16.19
Cl	27.24	31.78	−13.52	−10.63	26.91	34.48	−16.58	−7.59

From Figure 2, one can see that the geometric structures of RC, TS1, INT, and TS2 of the $H_3P{=}NH + H_2CO$ system in solution are identical with those in the gas phase. But the equilibrium structure of PC in solution is slightly different from that in the gas phase, namely, the former becomes tighter. The barriers of step 1 and step 2 in solution are 8.524 and 18.282 kcal/mol, respectively, and decrease compared with those values in gas phase (10.56 and 20.95 kcal/mol, respectively). The difference in free energy of solvation between RC and TS1 is −2.1 kcal/mol, and this indicates that TS1 is stabilized more by solvation than RC. For step 2, the TS2 is also stabilized by hydration compared with INT and has a free energy of solvation that is 1.43 kcal/mol smaller than that for INT. In aqueous solution, the free energies of activation of step 1 and step 2 for X = H are 10.94 and 18.27 kcal/mol, respectively. Thus, the decomposition of the intermediate (INT→TS2→PC) will become the rate-controlling step.

For the aza-Wittig reaction of $Cl_3P{=}NH$ with H_2CO in aqueous solution (see Figure 3), it can be observed along the reaction path that geometries of all minima are different from those in the gas phase. The reactant and product complexes become tighter. The intermediate has been shifted to an earlier stage of reaction. But the structures of two transition states are not affected by the solution. The barrier height of step 1 is 0.16 kcal/mol lower in aqueous solution than in gas phase and that of step 2 is 1.22 kcal/mol higher than in gas phase. From Table 6, it is found that the changes of free energy of activation from gas phase to solution are −0.33 and 2.70 kcal/mol for step 1 and step 2, respectively, and this indicates that TS1 is stabilized and TS2 is destabilized slightly by hydration. For step 2, the free energy of activation in water is 34.48 kcal/mol and is far larger than that for step 1 (26.91 kcal/mol). So step 2 is also the rate-determining step for X=Cl. Comparing the free energies of activation of rate-determining steps between two reactions (X= H and Cl) in aqueous solution, it can be concluded that the aza-Wittig reaction of $X_3P{=}NH$ with H_2CO in water carries out more favorably for X= H than X= Cl.

4. Conclusion

We have investigated the reaction mechanisms for the title aza-Wittig reactions of $X_3P{=}NH$ with $H_2C{=}O$ (X=H and Cl) using ab initio MP2/6-31G** level and IPCM method both in gas phase and in aqueous solution. Our results show that this reaction is a stepwise process with the first step as the rate-determining one in gas phase. The four-membered cyclic intermediate is the only intermediate for both X=H and Cl. The first and second forward barriers, with respect to the two transition states, increase in the order H< Cl in the gas phase. The results of the solvent effect calculations show that those two forward barriers decrease slightly by hydration. In aqueous solution, the second step of this reaction becomes the rate-controlling step for X=H and Cl because the energy barriers of step 2 are much higher than those of step 1. Obviously, the aza-Wittig reaction of $X_3P{=}NH$ with $H_2C{=}O$ can carry out more favorably for X=H than for X=Cl in the gas phase and in aqueous solution.

Acknowledgment. This work was supported by the National Natural Science Foundation of China (No. 29873030 and 20173036).

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