Theoretical Study of the $H_3PNH + H_2CO$ Reaction Mechanism via Five Reaction Channels

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Five reaction channels of the title reaction have been studied with the second-order Møller−Plesset perturbation theory by use of a split valence plus polarization 6-31G** basis set. The calculated results show that among the five channels the title reaction may favor the aza-Wittig and the addition routes. The aza-Wittig reaction $H_3PNH + H_2CO \rightarrow H_3PO + H_2CNH$ is shown as a two-step reaction via the first transition state, a four-membered ring intermediate, and then the second transition state. The first and the second forward barriers are 12.2 and 18.0 kcal/mol, respectively. The addition reaction $H_3PNH + H_2CO \rightarrow PH_2NHCH_2OH$ possesses only one transition state with a barrier of 13.3 kcal/mol.

1. Introduction

The iminophosphoranes, the key intermediates of the Staudinger reaction,[1−3] have drawn chemists' attention both experimentally and theoretically since the first synthesis by Staudinger and Meyer in 1919.[1] Mann and Chaplin prepared [*N*-(*p*-tolylsulfonyl)imino]triphenylphosphorane by the reaction of triphenylphosphine with chloramine-T.[4] Then other methods were developed, such as the Krisanov reaction[5] and the reaction of the ylides with Schiff's base.[6] The varied reactivity of the iminophosphoranes has been used extensively in organic synthesis.[7] As versatile reagents, they can carry on a series of interesting chemical reactions.

Since the iminophosphorane $R_3P{=}NR$ is isoelectronic with the Wittig reagent $R_3P{=}CR_2$ and also has the zwitterionic (ylide) character, it can likely react with the carbonyl compounds containing polarized oxygen via the aza-Wittig reaction,[8] e.g., $R_3P{=}NR + R_2CO \rightarrow R_3PO + R_2C{=}NR$. Such an aza-Wittig reaction may be much more significant in organic transformations, since it can introduce into the carbonyl compounds the imine (C=N) linkage that is labile and can be hydrolyzed and re-formed easily. However, in comparison with the extensively investigated Wittig reaction,[9−18] little attention is paid to the aza-Wittig reaction in both experimental and theoretical fields. In 1997, Jugo Koketsu and co-workers[19] studied first the aza-Wittig reaction of iminopnictoranes (H_3MNH, M = P, As, Sb and Bi) with formaldehyde at the MP2/DZ-d level. They came to the conclusion that the aza-Wittig reaction is more favorable for the P ylide than the As, Sb, and Bi ylides, where two reaction routes (the aza-Wittig and the Corey−Chaykovsky-type reactions) were taken into account.

To obtain more comprehensive information about the $H_3PNH + H_2CO$ reaction (especially to find out the competitive channels against the aza-Wittig route) and provide the theoretical basis for controlling the reaction runs, an attempt is made in this paper to investigate the following five reaction channels at the MP2/6-31G** level,

$$H_3PNH + H_2CO \longrightarrow H_3PO + H_2CNH \quad (1)$$

$$H_3PNH + H_2CO \longrightarrow PH_3 + NH_2CHO \quad (2)$$

$$H_3PNH + H_2CO \longrightarrow PH_3 + \underset{HN-CH_2}{\overset{O}{\triangle}} \quad (3)$$

$$H_3PNH + H_2CO \longrightarrow PH_2NHCHO + H_2 \quad (4)$$

$$H_3PNH + H_2CO \longrightarrow PH_2NHCH_2OH \quad (5)$$

where reaction 1 and reaction 3 correspond respectively to the aza-Wittig and the Corey−Chaykovsky-type channels[19] while reactions 2, 4, and 5 have not been studied before. Our present calculations show that the reaction channel is more favorable in the order reaction 1 ∼ reaction 5 > reaction 4 > reaction 3 > reaction 2, indicating that reaction 5 may be the most competitive channel against the aza-Wittig reaction. In addition, it is noticed that the aza-Wittig reaction surface calculated at the MP2/6-31G** level is somewhat different from that obtained at the MP2/DZ-d level;[19] only two of the three transition states at MP2/DZ-d can exist adequately at MP2/6-31G**.

2. Computational Methods

Ab initio molecular orbital calculations were performed with the GAUSSIAN 94 series of programs.[20] Geometries were fully optimized with the second-order Møller−Plesset perturbation theory using the standard split valence plus polarization 6-31G** basis set. The optimized geometries were used to compute the vibrational harmonic frequencies and zero-point corrections. It is known that minima are characterized by real frequencies, while transition states have one imaginary frequency. To confirm that the transition states connect properly the corresponding species, IRC calculations at MP2/6-31G** were carried out. Furthermore, in order to obtain more reliable total energies and activation barriers, the MP4/6-31G** energy calculations are performed using the MP2/6-31G** optimized geometries, and this kind of calculation is designated by the standard notation MP4/6-31G**//MP2/6-31G**.

3. Results and Discussions

To facilitate our discussions, the MP2/6-31G** optimized geometries of all of the reactants and products for reaction

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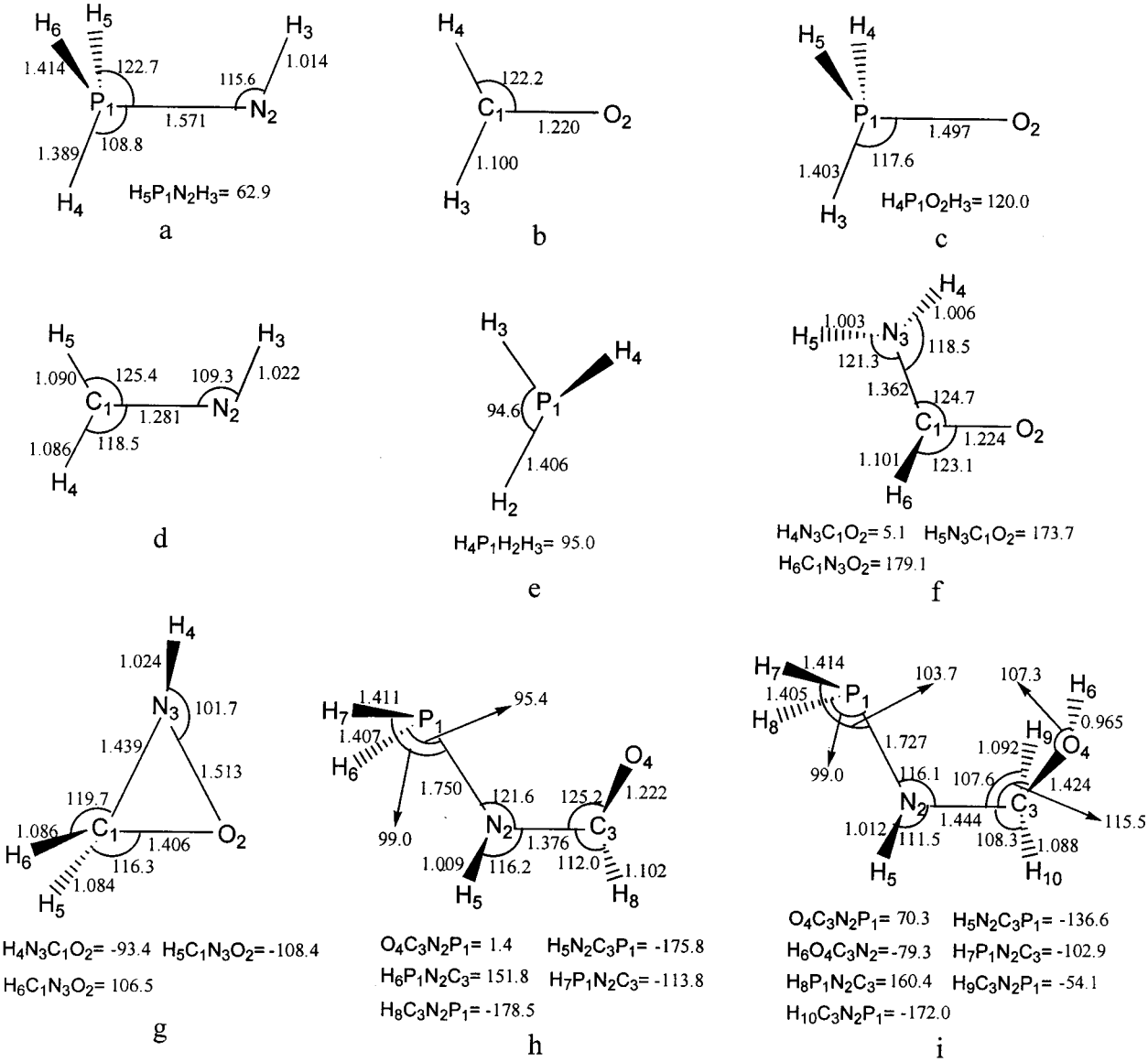

Figure 1. MP2/6-31G** optimized geometries of the reactants and products for reactions 1−5 (bond lengths in Å, angles in deg).

channels 1−5 are shown in Figure 1. For the iminophosphorane H_3PNH (Figure 1a), the P−N bond length calculated at MP2/6-31G** is 1.571 Å (while it is 1.571 Å at MP2/6-31G* [21] and 1.602 Å at MP2/DZ-d,[19] elsewhere). This value is consistent with the experimental P−N bond length of 1.574 Å for the (*N*-pyrid-4-ylimino)triphenylphosphorane (Ph_3PNPy).[22] To our knowledge, the geometries of H_2CO, H_3PO, H_2CNH, PH_3, NH_2-CHO, and the cyclic azaoxaridine, as shown in Figure 1b−g, have been studied at various calculation levels by previous investigators;[23−31] however, no study has yet been made on PH_2-NHCHO (Figure 1h) and PH_2NHCH_2OH (Figure 1i).

Reaction 1 (Aza-Wittig Reaction). The calculated results at MP2/6-31G** show that there exist two complexes (IC and IC1), two transition states (TS1a and TS1b), and one intermediate (IS) on the aza-Wittig reaction surface. As noted, at MP2/DZ-d, there are three transition states (T1, T2, and T3)[19] for the aza-Wittig reaction, where T1 and T3 correspond respectively to TS1a and TS1b at MP2/6-31G** in this paper. However, the pseudorotational transition state T2 connecting two rotational isomers of the intermediate cannot exist adequately at MP2/6-31G**. This difference can be attributed to the basis set effects. For MP2/DZ-d, the DZ-d basis set (used in ref 19) corresponds to LANL1DZ modified by five d-type functions (abbreviated as DZ-d), which is composed from D95V for first-row atoms and the Los Alamos effective core potentials (ECP) plus the valence double-ζ (DZ) basis functions for pnictogens. For MP2/6-31G**, the split valence plus polarization 6-31G** basis set consists of one size of basis function for each atomic orbital and two sizes of basis functions for each valence orbital. MP2/6-31G** does not contain the effective core potential approximation and therefore appears more accurate than MP2/DZ-d. Thus, it seems that T2 obtained at MP2/DZ-d may be an artifact.

The aza-Wittig reaction surface based on the present calculations can be simply expressed as $H_3PNH + H_2CO \rightarrow$ IC $\rightarrow$ TS1a $\rightarrow$ IS $\rightarrow$ TS1b $\rightarrow$ IC1 $\rightarrow H_3PO + H_2CNH$, which has been confirmed by the IRC calculations. The MP2/6-31G** optimized geometries of all the extrema on the reaction surface are shown in Figure 2, and the relative energies of these extrema are given in Table 1.

The reactant-like complex IC that also exists in reactions 2−5 is 4.8 kcal/mol lower in energy than the reactants $H_3PNH + H_2CO$ (Table 1). Since the complex IC lies in a shallow well on the potential energy surface, its stability in the gas phase should be examined by the corresponding change of the Gibbs free energy. For the same reason, the changes of the Gibbs free

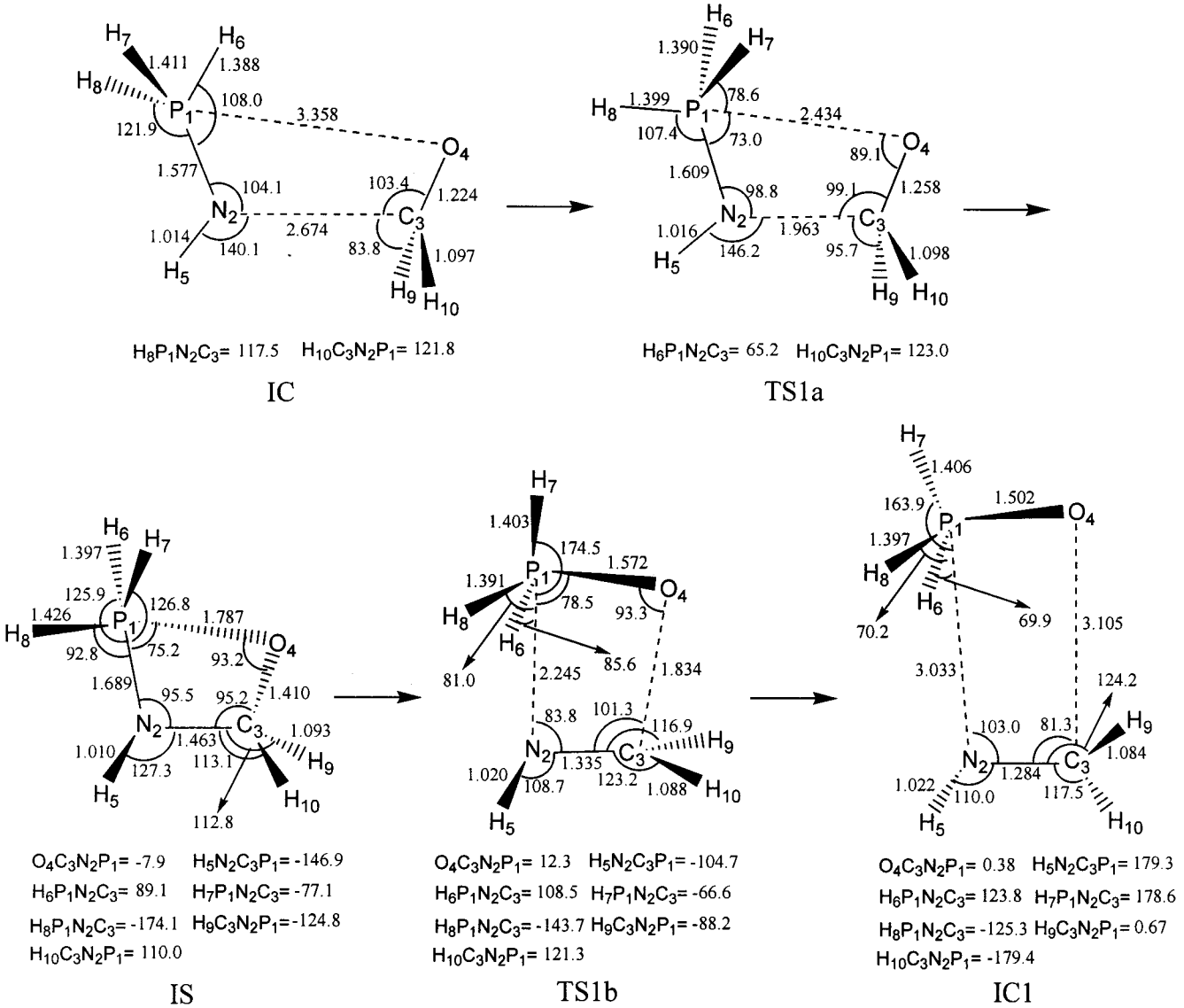

Figure 2. MP2/6-31G** optimized geometries of the complexes (IC and IC1), the transition states (TS1a and TS1b), and the intermediate (IS) for the aza-Wittig reaction (bond lengths in Å, angles in deg).

TABLE 1: Relative Energies with Respect to the Reactants $H_3PNH + H_2CO$ and Energy Barriers for the Aza-Wittig Reaction[a]

	relative energies	forward barriers	reverse barriers
IC	−4.8		
TS1a	7.4	12.2	23.9
IS	−16.5		
TS1b	1.5	18.0	31.6
IC1	−30.1		
$H_3PO + H_2CNH$	−24.4		

[a] MP4/6-31G**//MP2/6-31G** energies (kcal/mol) with zero-point correction based on the MP2 frequencies.

energies (at $T = 298.15$ K) for all the complexations in reactions 1−5 are calculated. As a result, the Gibbs free energy of IC is found 3.9 kcal/mol larger than that of the reactants $H_3PNH + H_2CO$, suggesting that in the gas phase IC may be unstable with respect to the dissociated reactants. Thus, the $H_3PNH + H_2CO \rightarrow$ IC process cannot be expected to proceed spontaneously; however, it may appear in the activation process of the reaction system since the calculated reaction path corresponds to the lowest energy path. As shown in Figure 2, the first transition state TS1a has a planar structure ($O_4C_3N_2P_1 = 0.0°$), while the $O_4C_3N_2P_1$ dihedral angle for the second transition state TS1b takes the value of 12.3°. The first and the second forward barriers with respect to TS1a and TS1b are 12.2 and 18.0 kcal/mol (Table 1). The four-membered ring intermediate IS existing between TS1a and TS1b is less stable than the products $H_3PO + H_2CNH$ by 7.9 kcal/mol. This energy difference implies that IS tends to decompose into the products from the thermodynamic viewpoint. To the end of the aza-Wittig reaction, IRC calculations show that the reaction will pass through a product-like complex IC1. The Gibbs free energy of IC1 is 3.3 kcal/mol larger than that of the products $H_3PO + H_2CNH$, suggesting that IC1 may be unstable in the gas phase and may decompose spontaneously into the products.

From the aza-Wittig reaction surface, it can be seen that in the gas phase the reaction can easily pass over TS1b, providing the reaction system has enough energy to cross TS1a. This is because TS1b is 5.9 kcal/mol lower in energy than TS1a (Table 1). However, the situation will be different in solution. Following the discussion of the solvation effects on the Wittig reaction,[9] we try to discuss similarly the situation in the aza-Wittig reaction. In solution, the interaction between the reacting molecules and solvent can make the excess energies of the reaction system disperse. In this case, the step corresponding

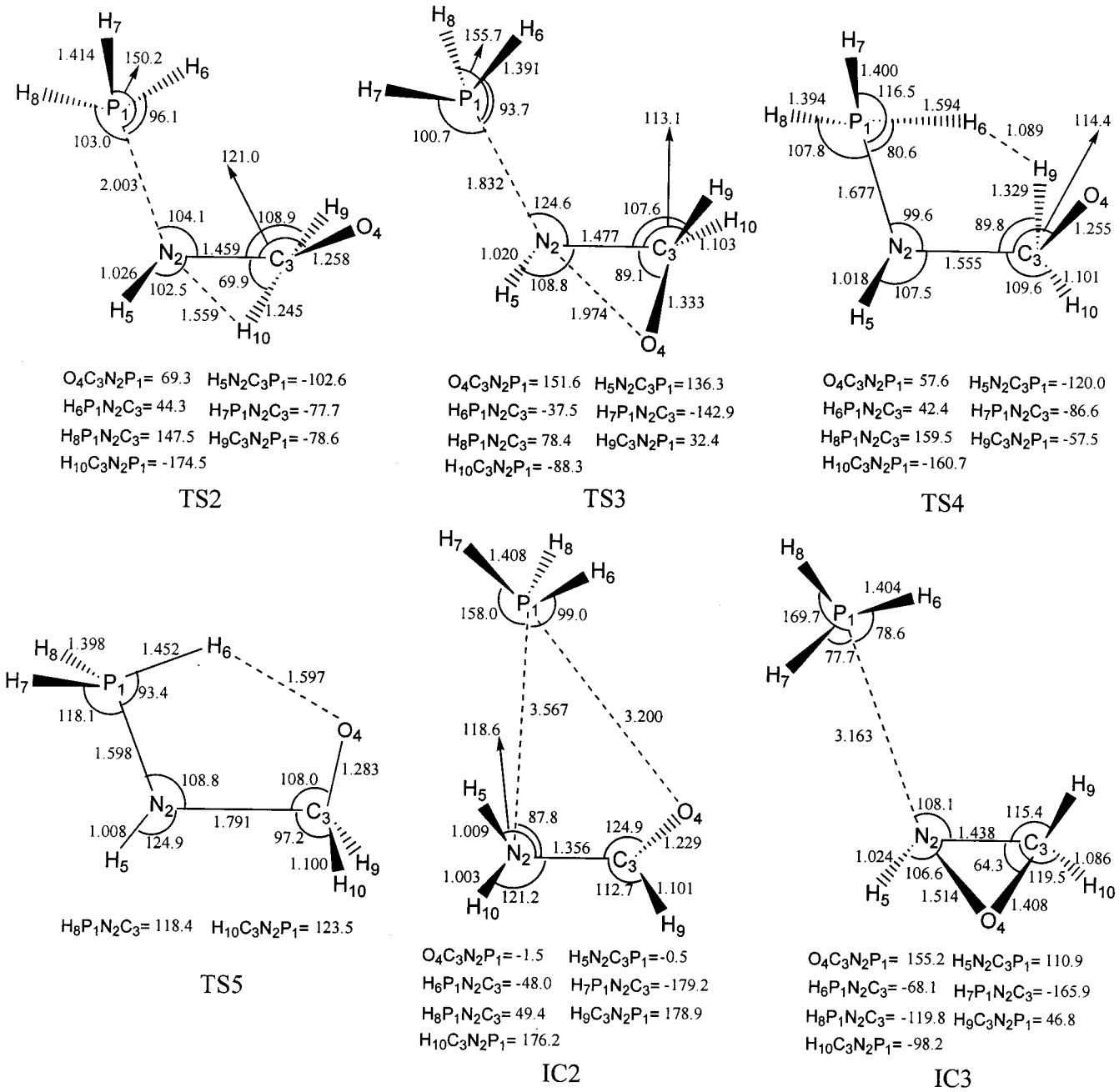

Figure 3. MP2/6-31G** optimized geometries of the transition states (TS2, TS3, TS4, and TS5) for reactions 2−5 and the product-like complexes (IC2 and IC3) for reactions 2 and 3 (bond lengths in Å, angles in deg).

to the highest reaction barrier on the whole aza-Wittig reaction surface will become the slowest (rate-determining) step. From the calculated dipole moments of TS1a (3.6 D) and TS1b (1.3 D), it is seen that TS1a is much more polar than TS1b. Thus, the stabilization by solvation is expected to be much larger for TS1a than for TS1b. This suggests that in solution the second forward barrier may remain higher than the first forward barrier and the decomposition of the intermediate via TS1b may become the rate-determining step.

Reactions 2, 3, 4, and 5. In comparison with the aza-Wittig reaction, each of reactions 2−5 has one transition state; i.e., they are all one-step reactions. Figure 3 shows the MP2/6-31G** optimized geometries of the transition states TS2, TS3, TS4, and TS5 with respect to reactions 2, 3, 4, and 5. It is seen from Figure 3 that the $O_4C_3N_2P_1$ dihedral angles for TS2, TS3, TS4, and TS5 take the values of 69.3°, 151.6°, 57.6°, and 0.0°, respectively.

As listed in Table 2, the activation barriers for reaction 2 and reaction 3 are 49.7 and 42.2 kcal/mol. The Corey-Chaykovsky-type reaction 3 to PH_3 + cyclic azaoxaridine is kinetically more favorable than reaction 2 to $PH_3 + NH_2CHO$. By the IRC calculations, reaction 2 and reaction 3 are shown to proceed via the product-like complexes IC2 and IC3, respectively. Again, the Gibbs free energies of IC2 and IC3 are respectively 5.1 and 4.1 kcal/mol larger than those of the corresponding dissociated products $PH_3 + NH_2CHO$ and PH_3 + cyclic azaoxaridine. As a result, IC2 and TC3 may decompose spontaneously in the gas phase. For reaction 4, the calculated activation barrier is 38.7 kcal/mol (Table 2), which is lower than both of reaction 2 and reaction 3. However, it is obvious that reactions 2−4 are all much disfavored than the aza-Wittig reaction.

Reaction 5 is the addition channel of the title reaction. TS5, the only transition state in reaction 5, has a planar structure

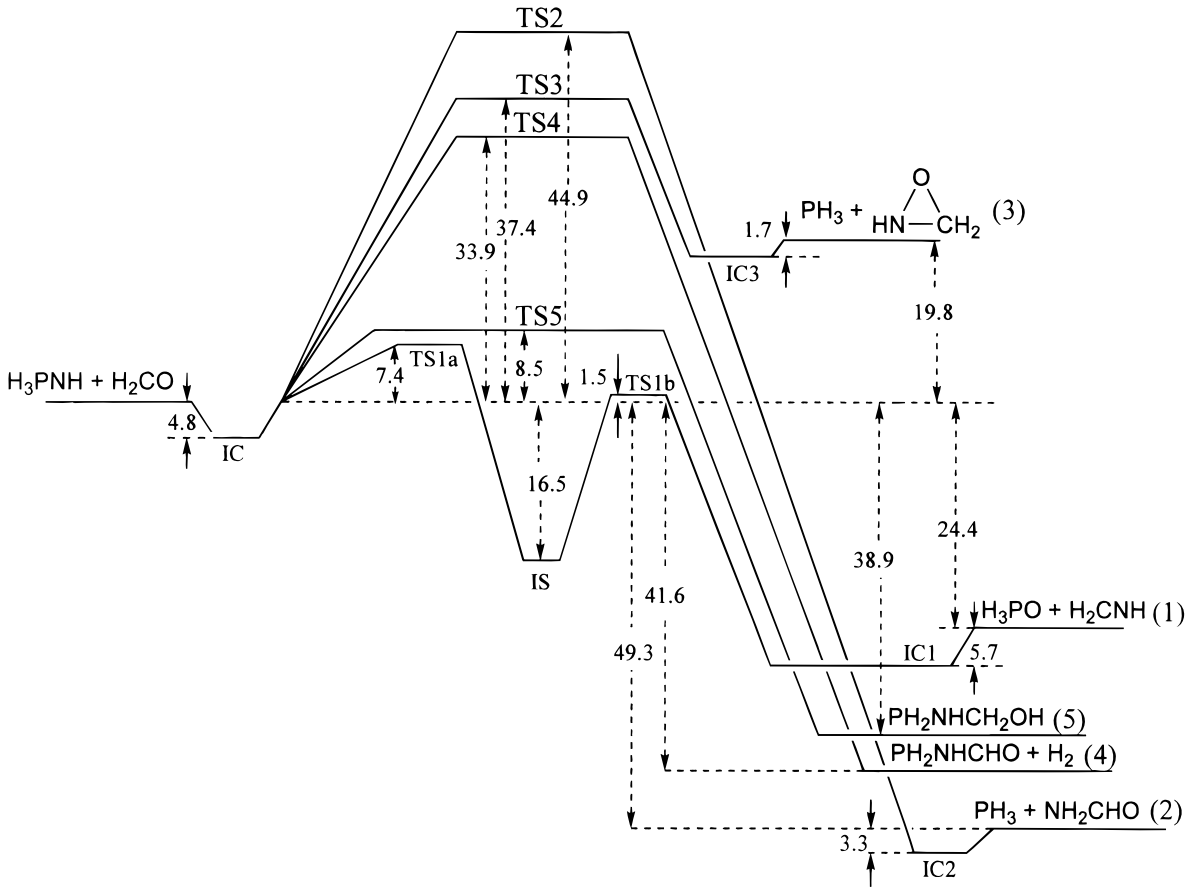

Figure 4. Schematic energy diagram (in kcal/mol) for reactions 1−5.

TABLE 2: Relative Energies with Respect to the Reactants $H_3PNH + H_2CO$ and Activation Barriers for Reactions 2−5[a]

		relative energies	activation barriers
reaction 2	TS2	44.9	49.7
	IC2	−52.6	
	$PH_3 + NH_2CHO$	−49.3	
reaction 3	TS3	37.4	42.2
	IC3	18.1	
	$PH_3 + HN{-}O{-}CH_2$	19.8	
reaction 4	TS4	33.9	38.7
	$PH_2NHCHO + H_2$	−41.6	
reaction 5	TS5	8.5	13.3
	PH_2NHCH_2OH	−38.9	

[a] MP4/6-31G**//MP2/6-31G** energies (kcal/mol) with zero-point correction based on the MP2 frequencies.

($O_4C_3N_2P_1 = 0.0°$), as does TS1a. The calculated activation barrier for reaction 5 is 13.3 kcal/mol (Table 2). It is much lower than the barrier heights for reaction 2 (49.7 kcal/mol), reaction 3 (42.2 kcal/mol), and reaction 4 (38.7 kcal/mol) and only 1.1 kcal/mol higher than the first forward barrier (12.2 kcal/mol) for the aza-Wittig reaction. To further investigate the two close barrier heights with respect to TS5 and TS1a, the CCSD(T)/6-311G** energy calculation is performed, and this also results in a small energy difference (1.1 kcal/mol) between TS5 and TS1a. Furthermore, the relative Gibbs free energies of TS5 and TS1a with respect to the reactants are calculated to be 17.8 and 17.0 kcal/mol, respectively, and these two Gibbs free energies are quite close. Therefore, reaction 5 may be the strong competitor against reaction 1, and PH_2NHCH_2OH (Figure 1i) that is 38.9 kcal/mol more stable than the reactants may be easily produced from reaction 5.

On the basis of the calculated results and the above discussions, it can be seen that the reaction channel is more favorable in the order reaction 1 ∼ reaction 5 > reaction 4 > reaction 3 > reaction 2. Correspondingly, Figure 2 and Figure 3 show that the C−N bond length is longer for TS1a (1.963 Å) > TS5 (1.791 Å) > TS4 (1.555 Å) > TS3 (1.477 Å) > TS2 (1.459 Å), indicating that the transition structures are more reactant-like in this order. Here, the geometry of TS1b cannot compare directly with other transition structures since its starting point is IS rather than IC. Now, we can arrive at the conclusion that the title reaction may favor the aza-Wittig and the addition routes, and $H_3PO + H_2CNH$ and PH_2NHCH_2OH produced from reaction 1 and reaction 5 may be the major products of the title reaction.

From Table 1 and Table 2, the relative electronic energies of the transition states are found to decrease in the order TS2 (44.9 kcal/mol) > TS3 (37.4 kcal/mol) > TS4 (33.9 kcal/mol) > TS5 (8.5 kcal/mol) ∼ TS1a (7.4 kcal/mol) > TS1b (1.5 kcal/mol). For the sake of comparison, the relative Gibbs free energies of the transition states with respect to the reactants are calculated to be in the order TS2 (58.1 kcal/mol) > TS3 (53.0 kcal/mol) > TS4 (44.6 kcal/mol) > TS5 (17.8 kcal/mol) ∼ TS1a (17.0 kcal/mol) > TS1b (11.7 kcal/mol). It can be easily seen that for the transition states the order of the electronic energies is consistent with that of the Gibbs free energies. In brief, the two inequality series for the transition states will lead to the same theoretical result. So, in this paper, we choose conventionally the electronic energies for our discussions of the reactions.

In addition, the relative energies of the products of the five channels (Table 1 and Table 2) inform us that reactions 1, 2, 4, and 5 are all exothermic while reaction 3 is endothermic. As a summary of the calculated results presented in this paper, the

schematic energy diagram, built up by Table 1 and Table 2, is shown in Figure 4.

4. Conclusions

In the present work, the title reaction with five reaction channels is studied in detail at the MP2/6-31G** level. The optimized geometries of all of the reactants, products, minima, and transition states for the five channels are obtained. The calculated results show that the aza-Wittig reaction is a two-step reaction via the first transition state (TS1a), a four-membered ring intermediate (IS), and then the second transition state (TS1b). The first forward barrier is 12.2 kcal/mol, and the second forward barrier is 18.0 kcal/mol. Reactions 2−5 are all shown as one-step reactions. The activation barriers for reactions 2−5 are 49.7, 42.2, 38.7 kcal/mol and 13.3 kcal/mol, respectively. It can be seen that the title reaction may favor reaction channels 1 and 5.

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