Theoretical study on the insertion reaction of the phosphenium cation and azirane

JINSONG GU, XIAODONG ZHAO, SHANKUI LIU and XIAOJUN TAN*

College of Biological Science and Technology, University of Jinan, Jinan, Shandong, 250022, People's Republic of China

Abstract: The mechanism of the insertion reaction between the phosphenium cation and azirane has been investigated theoretically in order to better understand the reactivity for the valence isoelectronic of carbene. The phosphenium cation acts as an electrophilic reagent and accepts the σ electrons of azirane to form a complex in the first combination step. The greater the positive charge on the phosphorus in the phosphenium cation, the more stable is the formed complex. Introduction of substituents will decrease the positive charge on the phosphorus in the phosphenium cation. The order of positive charge on phosphorus is HP^+–F > HP^+–OH > HP^+–NH_2, which is consistent with their Lewis acidities. The complex transforms to a four-membered ring product *via* a transition state in the second insertion step. The product is more stable than the complex due to the decrease of the ring extension.

Keywords: electrophilic reagent; carbene; silylene.

INTRODUCTION

The phosphenium cation (R_2P^+) is valence isoelectronic and isolobal with carbene (R_2C), silylene (R_2Si) and the nitrenium cation (R_2N^+).[1,2] The simplest phosphenium cation is H_2P^+, which contains a positive charged phosphorus center and two hydrogens. H_2P^+ is detected through photoionization of PH_3 and other phosphorus-bearing compounds.[3] The ground state of H_2P^+ is a singlet, the energy gap of singlet–triplet is about 67 kJ m^{-1}.[4] The hybridization of the central phosphorous atom can be regarded as being sp^2, with a lone electron pair in the filled sp^2 orbital and a vacant p orbital.[5] Introduction of a variety of substituents has been used to prepare and isolate stable phosphenium cations. The diamino-methylphosphenium cation, $(NMe_2)_2P^+$, is the first stable, isolable cation in low--coordinated phosphorus chemistry.[6] Later, other stable phosphenium cations

have been characterized successively, for example the phosphanetriylammonium cation (MeN=P$^+$)[7] and methylenephosphenium cation (Me$_2$C=P$^+$).[8]

The chemistry of different species tends to be dominated by their electrophilic behaviour, a key concern is their Lewis acidities. The fluoride ion affinities (FIAs) can act as a measure of the Lewis acidities of phosphenium cations.[9] Slattery *et al.* calculated the FIAs of 33 phosphenium cations with a range of substituents. The results demonstrated that phosphenium cations are often stronger Lewis acids than neutral species, but in many cases are less Lewis acidic than highly electrophilic cations such as [Me$_3$C]$^+$ or [Me$_3$Si]$^+$.[10] The dipole moments of PH$_2$$^+$ and other compounds containing silicon or phosphorus have been computed to evaluate the intensities of rotational transitions and reactivity.[11]

The chemical reactions of the phosphenium cation are similar to its carbon-based and silicon-based analogues, including cycloaddition reaction, C–H insertion reaction, *etc.*, making them versatile reagents in some kinds of transformations and reactions.[12–14] The phosphenium cation can be applied as ligands in coordination chemistry, acting as the building blocks in phosphorus-bearing compounds.[15] In addition, as a class of strongly π-accepting ligands, phosphenium cation can be used in homogeneous catalytic systems.[16]

The reactions of carbene and silylene have been extensively investigated. The reactions of the phosphenium cation have also attracted attentions.[17,18] Since the phosphenium cations have a vacant p orbital and a filled sp^2 orbital, they can act as both Lewis acids and Lewis bases, respectively. Phosphenium cation can participate in complexation reactions with metals where it acts as a Lewis base,[19,20] or in cycloaddition reactions with alkynes where it acts as a Lewis acid.[21] In the present study, we performed a comprehensive theoretical investigation of the reaction between phosphenium cation and azirane was performed. The reaction mechanism has been described and the effects of a variety of substituents in phosphenium cation have been evaluated. The present results will enrich the available data for the relevant phosphenium cation chemistry and will provide more information for expanding its application in coordination chemistry and catalytic systems.

CALCULATION METHOD

For the reaction between phosphenium cation and azirane, the popular hybrid density functional (B3LYP)[22,23] with 6-311++G** and aug-cc-pVTZ basis sets were employed to locate all the stationary points along the reaction pathway without imposing any symmetry constraints. The reliability and efficiency of this method in predicting the geometries and properties have been verified by a number of investigations.[24,25] Frequency analyses was conducted to confirm the nature of the minima and transition state. Moreover, intrinsic reaction coordinate (IRC) calculations were also performed to further validate the calculated transition state connecting reactant and product. Additionally, the relevant energy quantities, such as reaction energies and barrier heights, were corrected with zero-point vibrational energy (ZPVE) corrections.

To further refine the calculated energy parameters, single-point energy calculations were performed at the CCSD(T)/6-311++G** level of theory based on the stationary points optimized by the corresponding B3LYP method. As described below in Fig. 1 and Table I, several kinds of computational levels can give approximately consistent results for the optimized structures and the calculated reaction profile of the reaction between H_2P^+ and azirane. Therefore, for the reaction of substituted phosphenium cation (HXP^+) and azirane, the B3LYP method in conjunction with the 6-311++G** basis set was performed to confirm the nature of the minima and transition state as well as the energy parameters. For the sake of simplicity, for all the reactions, the energy results at the B3LYP/6-311++G** level were mainly discussed below if not noted otherwise.

All the calculations were performed using the Gaussian 09 program.[26] Matrixes of whole optimized structures are given in Supplementary material to this paper.

RESULTS AND DISCUSSIONS

For the insertion reaction of phosphenium cation and azirane, the first step was the formation of a complex (Com) without barrier. The second step was the isomerization of Com to a product (Pro) *via* a transition state (TS). The geometric parameters for the reactants (R1-H_2P^+ and R2-azirane), Com, TS and Pro involved insertion reaction are displayed in Fig. 1. The corresponding energies are listed in Table I.
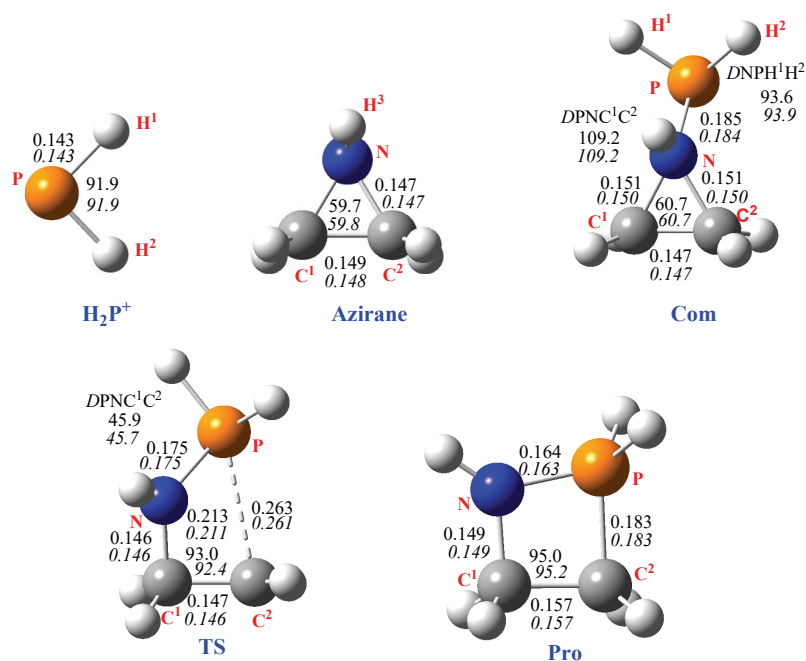

Fig. 1. Optimized structures of the reactants (H_2P^+, azirane), complex (Com), transition state (TS), and product (Pro) in the insertion reaction at the B3LYP/6-311++G** (first line) and B3LYP/aug-cc-pVTZ (second line, *italic*) level of theory, where the bond length and bond angle (and dihedral angle) are in nm and degree, respectively.

TABLE I. The calculated relative energies (kJ mol^{-1}) in the reaction of phosphenium cation (H_2P^+) and azirane with respect to the isolated reactants at the three calculated levels of theory considering the ZPVE corrections

Species	B3LYP/6-311++G**	CCSD(T)//B3LYP/6-311++G**	B3LYP/aug-cc-pVTZ
Com	–405.8	–407.0	–424.6
TS	–242.6	–246.0	–230.0
Pro	–425.7	–437.3	–435.4

When phosphenium cation approaches to the N atom of azirane, it can form a complex (Com) with azirane, which is a barrier-free process. In the Com, the configuration of azirane fragment changed slightly compared with that in isolated azirane. The bond length of C^2–N in the Com prolonged slightly by 0.003 nm than that in isolated azirane, denoting a weakening of the C^2–N bond. To investigate the combination process of phosphenium cation and azirane, the potential energy curve for the Com was constructed along the distance between the two fragments. As displayed in Fig. 2, the energy of the system decreases continuously before the combination of PH_2^+ and azirane. After the equilibrium point (here the N–P bond is 0.185 nm), the energy will be increased rapidly as PH_2^+ and azirane approach each other.
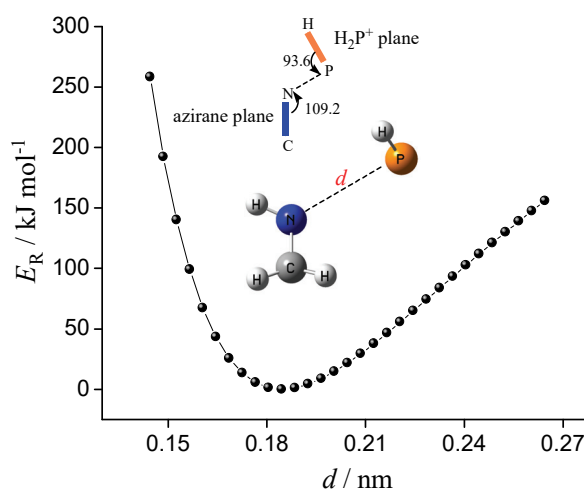

Fig. 2. Energy changes in the combined process of complex along with the distance between two fragments at the B3LYP/6-311++G** level of theory.

The combination process can be understood through interaction of the frontier molecular orbital theory. As displayed in Fig. 3, the frontier orbitals for LUMO of H_2P^+ and HOMO of azirane are symmetrically matching. As H_2P^+ initially interacts with azirane, the 3p unoccupied orbital of phosphorus in H_2P^+ inserts into the sp^3 orbital of azirane to form a σ→p donor–acceptor bond, resulting in the formation of the Com. The dihedral angle of PNC^1C^2 (109.2°) is iden-

tical with the angle of normal sp^3 orbitals (109.28°), which proves the mechanism described above. As an electrophilic reagent, H_2P^+ accepts σ electrons from azirane in the combination process. The greater the positive charge on phosphorus atom in H_2P^+, the easier the formation of the σ→p donor–acceptor bond will be and therefore, the more stable will the formed complex be.
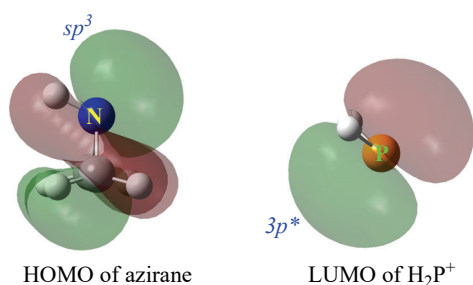

Fig. 3. The calculated LUMO orbital for H_2P^+ and the HOMO orbital for azirane.

For the sake of better understanding the combination process of phosphenium cation and azirane, the effect of variety of substituents was considered, which are marked with superscript "X". The geometric parameters for the ^{X}Com, ^{X}TS, and ^{X}Pro are listed in Table II, The corresponding energies are listed in Table III.

TABLE II. The geometric parameters for the species involved in the insertion reaction of substituted phosphenium cation (HXP$^+$) and azirane

Geometry	X	Bond length, nm						Bond angle, °	
		P–X	N–P	C^{1}N	C^{2}N	C^{1}C^2	C^{2}P	$\angle$NC^{1}C^2	DPNC^{1}C^2
^{X}Com	F	0.161	0.184	0.151	0.151	0.147	0.292	61.0	109.6
	CH$_3$	0.184	0.186	0.150	0.150	0.147	0.292	60.7	109.2
	OH	0.163	0.187	0.150	0.151	0.147	0.295	60.8	109.6
	OCH$_3$	0.162	0.189	0.150	0.150	0.147	0.296	60.7	109.2
	NH$_2$	0.166	0.193	0.150	0.150	0.148	0.297	60.7	108.6
	NHCH$_3$	0.165	0.196	0.149	0.150	0.148	0.300	60.6	108.2
^{X}TS	F	0.160	0.173	0.147	0.210	0.147	0.261	90.9	50.2
	CH$_3$	0.183	0.176	0.147	0.209	0.147	0.263	90.9	48.2
	OH	0.163	0.175	0.147	0.209	0.147	0.262	90.5	49.6
	OCH$_3$	0.162	0.175	0.147	0.208	0.147	0.263	90.2	50.4
	NH$_2$	0.167	0.175	0.147	0.211	0.147	0.268	91.9	52.1
	NHCH$_3$	0.167	0.175	0.147	0.212	0.147	0.271	92.1	53.4
^{X}Pro	F	0.157	0.161	0.150	0.226	0.157	0.181	94.7	5.2
	CH$_3$	0.180	0.165	0.149	0.226	0.157	0.183	95.0	−9.2
	OH	0.159	0.163	0.150	0.225	0.157	0.181	94.7	2.9
	OCH$_3$	0.157	0.163	0.149	0.225	0.157	0.181	94.7	3.3
	NH$_2$	0.163	0.164	0.149	0.225	0.156	0.183	94.7	−6.9
	NHCH$_3$	0.163	0.164	0.149	0.225	0.156	0.184	94.8	−7.3

TABLE III. The calculated Mulliken charge of the phosphorus atom in HXP$^+$ and the relative energies in the reaction of substituted phosphenium cation and azirane at the B3LYP/6--311++G** level of theory considering the ZPVE corrections

Species (HXP$^+$)	Mulliken charge of P in ^{X}R1	Relative energy, kJ mol^{-1}		
		^{X}Com	^{X}TS	^{X}Pro
H–P$^+$–H	0.955	–405.8	–242.6	–425.7
H–P$^+$–F	0.914	–373.1	–235.7	–427.4
H–P$^+$–CH$_3$	0.807	–325.8	–173.4	–382.0
H–P$^+$–OH	0.751	–289.7	–146.1	–346.5
H–P$^+$–OCH$_3$	0.672	–248.1	–105.5	–312.4
H–P$^+$–NH$_2$	0.644	–210.8	–59.8	–265.2
H–P$^+$–NHCH$_3$	0.555	–174.8	–24.9	–230.9

As displayed in Table III, for the substituted HXP$^+$, the greater the positive charge on phosphorus in phosphenium cation, the more stable the formed complex will be. Take the substituted HP$^+$–OH as an example, both the phosphorus and oxygen are in sp^2 hybridization. The unoccupied p orbital of phosphorus and occupied p orbital of oxygen are in parallel. The two p orbitals overlap to form a π bond, in which some electrons on oxygen transferred to phosphorus, resulting in a decrease in the positive charge of phosphorus in HP$^+$–OH. The greater the electronegativity, the greater is the ability of bounding electron, therefore, the less the electrons are transferred to phosphorus. The electronegativity order of elements in the second period is F > O > N > C, therefore, the order of positive charge on phosphorus should be HP$^+$–F > HP$^+$–OH > HP$^+$–NH$_2$ > HP$^+$–CH$_3$, which is in good agreement with the calculated results, with an exception of HP$^+$–CH$_3$. The reason is that the carbon in the –CH$_3$ group is in sp^3 hybridization and hence, cannot form a π bond with the unoccupied p orbital of phosphorus, which limits the transfer of electron from C to P. In addition, the fluorine in HP$^+$–F is also in sp^3 hybridization. The sp^3 hybridization combined with highest electronegativity, the electron on fluorine can't transfer to phosphorus, which results in highest positive charge on the fluorine in HP$^+$–F. As shown in Fig. 4, there is a simple linear relationship between relative energy of ^{X}Com and positive charge on phosphorus of HXP$^+$.

The order of the positive charge density in the substituted phosphenium cation is consistent with the order of their Lewis acidities reported by the Slattery group.[10]

The Com transforms to the Pro *via* a ring-expanding process with a barrier of 163.2 kJ mol^{-1}. The unique imaginary frequency calculated for the corresponding TS is 512i cm^{-1} at the B3LYP/6-311++G** level of theory.

As shown in Fig. 1, the distance of C^2–P in TS is 0.263 nm, indicating the new bond of C^2–P is to be formed. Simultaneously, the C^2–N distance in the R2 fragment of TS reached 0.213 nm, which is greatly elongated than that in Com.

Therefore, based on the bond length data, the single bond of C^2–N in Com is to be broken *via* TS. The formation of the new σ bond of C^2–P and the break of σ bond of C^2–N occurred simultaneously. The Pro is a four-membered ring compound, bearing phosphorus and nitrogen, which is stabilized by 19.9 kJ mol^{-1} compared to the three-membered Com.
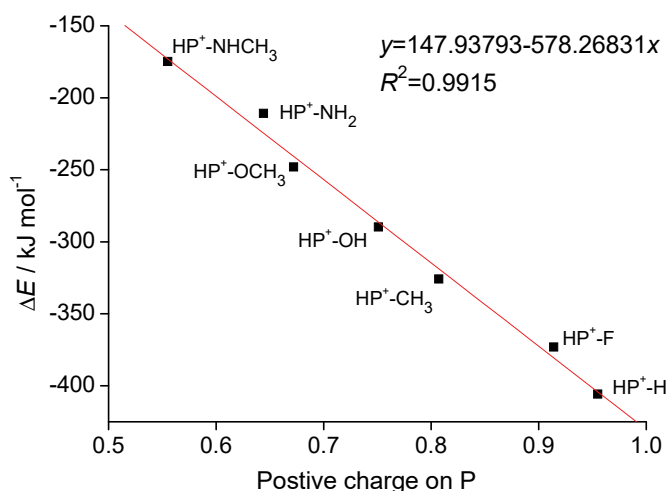

Fig. 4. The relationship between relative energy of ^{X}Com and the positive charge on the phosphorus of HXP$^+$.

CONCLUSIONS

In the present study, the insertion reaction between the phosphenium cation and azirane has been comprehensively investigated employing the B3LYP theoretical method with 6-311++G** and aug-cc-pVTZ basis sets. The first step of the reaction is the formation of a complex without barrier. H_2P^+ acts as an electrophilic reagent and accepts the σ electrons of azirane in the combination process. The greater the positive charge on the phosphorus in the phosphenium cation, the more stable is the formed complex. Introduction of substituents will decrease the positive charge on the phosphorus in the phosphenium cation. The order of positive charge of phosphorus is HP$^+$–F > HP$^+$–OH > HP$^+$–NH$_2$, which is consistent with their Lewis acidities. Therefore, introduction of substituents will decrease the stability of the complex. The complex transforms to a four--membered ring product *via* a transition state. The product is more stable than the complex due to the decreased ring-tension.

SUPPLEMENTARY MATERIAL

Matrixes of whole optimized structures are available electronically at the pages of journal website: https://www.shd-pub.org.rs/index.php/JSCS/article/view/11539, or from the corresponding author on request.

ИЗВОД

ТЕОРИЈСКО ПРОУЧАВАЊЕ РЕАКЦИЈЕ УГРАДЊЕ ФОСФЕНИЈУМ КАТЈОНА НА АЗИРАН

JINSONG GU, XIAODONG ZHAO, SHANKUI LIU и XIAOJUN TAN

College of Biological Science and Technology, University of Jinan, Jinan, Shandong, 250022, People's Republic of China

Механизам реакције уградње фосфенијум катјона у азирен проучен је теоретски како би се боље разумела реактивност интермедијера валентно изоелектронским са карбеном. Фосфенијум катјон делује као електрофилни реагенс и прихвата σ електроне азирана формирајући комплекс у првом ступњу комбиновања. Што је веће позитивно наелектрисање на фосфору у фосфенијум катјону, то је формирани комплекс стабилнији. Увођење супституената ће смањити позитивно наелектрисање на фосфору у фосфенијум катјону. Редослед позитивних наелектрисања на фосфору је $HP^+-F > HP^+-OH > HP^+-NH_2$, што се слаже са Лусовим киселостима. Комплекс се трансформише у производ са четворочланим прстеном преко прелазног стања у другом ступњу уградње. Производ је стабилнији од комплекса због смањења напона у прстену.

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