

Theoretical study of the insertion reaction of singlet phosphinidene with hydrogen sulfide

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The mechanism of the insertion reaction of singlet phosphinidene with hydrogen sulfide has been studied at HF/6-31G(d), MP2(full)/6-31G(d) and CCSD(T)/6-311 + G(d, p) levels, taking place through a three-membered ring transition state. The thermodynamic and kinetic properties of this reaction channel in the temperature range of 100–1500K have been studied, and it is concluded that the reaction is thermodynamically favoured at low temperature and kinetically favoured at high temperature.

Keywords: insertion reactions, phosphinidene, hydrogen sulfide

Increased attention has been paid over recent years to the chemistry of phosphinidene, which is an analogue of the better-known carbene, both experimentally and theoretically, for it plays an important role in the field of chemical catalysis, elementary chemistry and organometallic chemistry.^{1–4} Free phosphinidene and its substituted analogues are unstable and short-lived species. The detection of mesitylphosphinidene using ESR spectroscopy was reported by Li *et al.*,⁵ establishing the existence of RP as free transient species. Szieberth *et al.*⁶ computed the heats of formation of phosphinidene and its substituents, and Park and Pierini *et al.* have studied the proton affinities, molecular properties and valence state of phosphinidene.^{7,8} Goto *et al.* observed the lowest rotational spectral lines of the phosphinidene radical in its ground vibronic state by submillimetre-wave spectra.⁹ Examination of the lowest energy triplet and singlet electronic configuration of phosphinidene reveals its analogy with carbene. Both are very reactive, having condensation reactions with a great variety of partners.^{10,11} Mathey *et al.* developed several synthetic methods for the generation and trapping of terminal phosphinidene complexes in their prolific work.^{12–15} They have reported the reaction mechanism of alkene addition of the complexes (R–P–M(CO)₅, R = H, Ph, OCH₃, NEt₂; M = Cr, Mo, W), and found their electrophilic carbene-like nature. It is then natural to wish to know the reactivity and stability of the uncomplexed parent phosphinidene, and whether it also could display carbene-like character.

In the present work, a systematic theoretical study on the insertion reaction of singlet phosphinidene with polar molecule

hydrogen chloride was carried out in detail at HF/6-31G(d), MP2(full)/6-31G(d) and CCSD(T)/6-311 + G(d, p) levels. Due to the preparative difficulty, experimental information on basic spectroscopic, kinetic and thermodynamic parameters of free phosphinidenes is very scarce. Therefore we attempt to provide such information, and further calculations of thermodynamic and kinetic characters of the insertion reaction at different temperatures have been introduced in our work within the temperature range of 100–1500K, in steps of 200K, in order to obtain a better understanding of the reactivity of singlet phosphinidene and the influence of temperature on this.

Computational methods

All *ab initio* molecular orbital calculations were carried out by using the Gaussian 03 series of programs.¹⁶ We have calculated the total energies and relative energies at MP2(full)/6-31G(d), MP4SDQ/6-311 + G(d,p) and CCSD(T)/6-311 + G(d, p) levels. The optimised geometries and Milliken electronic populations of all structures were obtained at HF/6-31G(d) and MP2(full)/6-31G(d) levels, and their frequencies were calculated at the HF/6-31G(d) level to judge the nature of stationary points, which were subsequently used to calculate the thermodynamic and kinetic functions. The minimum energy path (MEP) was followed in both forward direction and reverse direction using the intrinsic reaction coordination (IRC) method at the same level in order better to ascertain the reaction pathway. On the other hand, by using general statistical thermodynamics and Eyring transition state

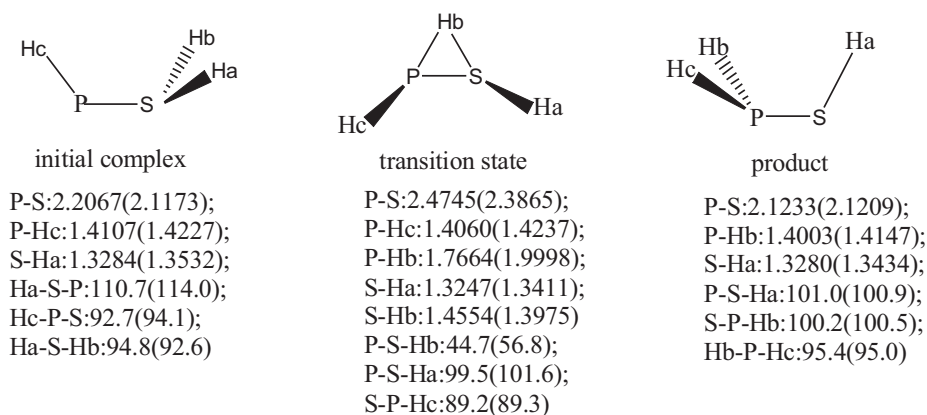


Fig. 1 Structure diagrams of the initial complex, transition state and product at HF/6-31G(d)(MP2(full)/6-31G(d)) level (bond distances and bond angles are in units Å and deg., respectively).

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theory with Wigner correction, we examined the influence of temperature on the reaction channel. All computations of the thermodynamic and kinetic parameters (ΔH° , ΔG° , ΔS° , K , k , A) were obtained using a homemade program, and the CCSD(T)/6-311 + G(d, p) energies were used as the electronic energy contribution.

Results and discussion

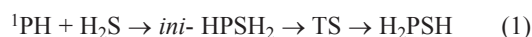
On account of its electron configuration, singlet phosphinidene has two σ -electron pairs and one empty p-orbital in the valence shell, so it may be nucleophilic due to the σ -electron pairs, and electrophilic due to the vacant p-orbital, and we should obtain its σ -complexes and p-complexes, respectively. The dual properties can lead to reactive complexity of singlet phosphinidene when it reacts with polar covalent compounds and ionic compounds, so we have chosen the polar molecule hydrogen sulfide to react with singlet phosphinidene in the present study. Both HF/6-31G(d) and MP2(full)/6-31G(d) structures for initial complex, product and transition state are shown in Fig. 1.

We have obtained one initial complex HPSH₂, which has C_s symmetry. At HF/6-31G(d) level its bond angle H_a-S-H_b (94.8°) is slightly greater than that of H-S-H (94.4°) in the H₂S molecule, and HP receives 0.247e from H₂S. The bond angle value of S-P-H_c is 92.7°, which is close to 90.0°. The total energies for all species and their relative energies are listed in Table 1.

The complexation energy of HPSH₂ is 25.8 kcal/mol at the CCSD(T)/6-311 + G(d, p) level. The results suggest that HPSH₂ is formed by insertion of the electrons of S atom in the H₂S molecule into the empty P p-orbital and singlet phosphinidene displays very strong electrophilic behaviour in its insertion of hydrogen sulfide. Therefore the initial complex HPSH₂ can be called a p-complex. The transition state has been found, and it has only one imaginary frequency 1126.99i at HF/6-31G(d) level, which confirms the saddle point characters and corresponds to its local maximum stationary structure, *i.e.* the transition state. The others are real frequencies, suggesting their local minimum stationary structures. In the transition state structure, the H_b-S distance is 1.4554 (1.3975) Å at HF/6-31G(d)(MP2(full)/6-31G(d)) level, and the H_b-P distance and its bond order at HF/6-31G(d) level are 1.7664 Å and 0.1396, respectively. These findings lead to the conclusion that transition state is a three-membered ring structure and is formed by inserting the electrons of the S atom of H₂S into

the empty P p-orbital and attack of the H atom of H₂S to the P lone pair.

In order to confirm the reactant and the product connecting the obtained transition state, IRC calculations have been undertaken at HF/6-31G(d) level, and we find the reaction path that is as follows:



This reaction channel has been revealed by Sudhakar and Lammertsma.¹⁷ However, it is well known that every chemical reaction takes place at a certain temperature, and in order to understand this insertion reaction channel more fully, we used a home-made program to examine more fully its thermodynamic and kinetic properties. The program is based on the general statistical thermodynamics and Eyring TS theory with Wigner correction. The variation of the thermodynamic and kinetic parameters with temperature is given in Table 2.

The enthalpy changes ΔH° , the Gibbs free energy changes ΔG° and the entropy changes ΔS° are all negative over the range 100–1500K. Therefore this insertion reaction path is an exothermic and spontaneous process over which the entropy decreases. Its equilibrium constants (K) are very large over the temperature range, especially at low temperature, and decrease rapidly with increase of temperature, so it can be concluded that the reaction is thermodynamically favoured at low temperature.

In addition, we calculated kinetic parameters, the A factors and the reaction rate constants k , in order to reveal the probabilities of this reaction. The rate constant expression can be written as:

$$k^{\text{TST/W}} = g(k_B T/h) \exp(\Delta S_m^\ddagger/R - \Delta H_m^\ddagger) \quad (2)$$

$$g = 1 + 1/24/(h\nu^\ddagger/k_B T)^2 \quad (3)$$

$$A = g(k_B T/h) \exp(\Delta S_m^\ddagger/R) \quad (4)$$

where g is the Wigner correction factor; k_B and h are Boltzmann and Planck constants, respectively; R is the ideal gas constant; and ν^\ddagger is the imaginary frequency of the transition state; ΔS_m^\ddagger and ΔH_m^\ddagger are the standard entropy and enthalpy of activation for the system, respectively. We can find from Table 2 that all log A values of this reaction are nearly equal to 13, which indicates that it belongs to an Arrhenius-type reaction, and that the reaction rate constant k increases sharply at low

Table 1 Total energies and relative energies E_{rel} for examined species^a

Structure	MP2(full)/6-31G(d)	MP4SDQ/6-311 + G(d, p)	CCSD(T)/6-311 + G(d, p)	E_{rel}^b
PH + H ₂ S	-740.079198	-740.199888	-740.215312	0.0
HPSH ₂	-740.135370	-740.245436	-740.256376	-25.8
H ₂ PSH	-740.212877	-740.321701	-740.331252	-72.8
TS	-740.102457	-740.221289	-740.233391	-11.3

^aTotal energies in hartree, and relative energies in kcal/mol.

^b E_{rel} is calculated by CCSD(T)/6-311 + G(d,p) energies.

Table 2 The thermodynamic and kinetic data for the insertion reaction within the temperature range of 100K–1500K (ΔH° , ΔG° and ΔS° have units of kJ mol⁻¹)

Reaction	T(K)	ΔH°	ΔG°	ΔS°	K	$k(\text{s}^{-1})$	$A(\text{s}^{-1})$
HPSH ₂ →	100	-195.30	-195.17	-1.37	0.88×10^{102}	0.54×10^{-11}	0.66×10^{13}
	300	-195.92	-194.58	-4.47	0.76×10^{34}	0.10×10^6	0.25×10^{14}
TS→	500	-196.51	-193.51	-6.01	0.16×10^{21}	0.22×10^9	0.36×10^{14}
	700	-196.81	-192.24	-6.53	0.22×10^{15}	0.68×10^{10}	0.45×10^{14}
H ₂ PSH	900	-196.95	-190.92	-6.70	0.12×10^{12}	0.47×10^{11}	0.52×10^{14}
	1100	-197.00	-189.57	-6.75	0.10×10^{10}	0.17×10^{12}	0.57×10^{14}
	1300	-197.01	-188.22	-6.76	0.36×10^8	0.41×10^{12}	0.61×10^{14}
	1500	-197.00	-186.87	-6.75	0.32×10^7	0.80×10^{12}	0.64×10^{14}

temperature, and then rises gradually at high temperature; k is $0.54 \times 10^{-11} \text{ s}^{-1}$ at 100K and $0.80 \times 10^{12} \text{ s}^{-1}$ at 1500K, which means that it is kinetically favoured at high temperature. Because of the scarcity of experimental information on the basic spectroscopic, kinetic and thermodynamic parameters, on account of the preparative difficulty, our present work might be useful for filling the missing information.

Conclusions

From the investigations reported in this paper, we can draw the conclusions based on theoretical calculations as follows:

(1) Starting from the initial complex HPSH_2 , which is a stable intermediate and is the initial association between singlet phosphinidene with hydrogen sulfide, this discussed reaction channel belongs to insertion reaction with a three-membered ring transition state and yield the product H_2PSH .

(2) The thermodynamic and kinetic calculations of the reaction reveal that: with the rise of the temperature, the equilibrium constant K decreases sharply, while the reaction rate constant k increases slowly. This reaction is thermodynamically favoured at low temperature and kinetically favoured at high temperature.

Free phosphinidene has only been observed as short-lived species in dilute gas phase or in matrices at low temperature.⁵ Especially, the direct experimental measurements of the thermodynamic and kinetic parameters for this reaction are very insufficient at present. Therefore, we think that the research results based on quantum calculations and thermodynamic and kinetic calculations in this work will provide useful predictions for later experimental research work.

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