Vol. 45 No. 1 SCIENCE IN CHINA (Series B) February 2002

Structures and stabilities of HPO_2 isomers

YU Haitao (于海涛)[1,2], CHI Yujuan (池玉娟)[1], FU Honggang (傅宏刚)[1,2], HUANG Xuri (黄旭日)[2], LI Zesheng (李泽生)[2] & SUN Jiazhong (孙家钟)[2]

1. College of Chemistry and Chemical Engineering, Heilongjiang University, Harbin 150080, China;
2. State Key Laboratory of Theoretical and Computational Chemistry, Institute of Theoretical Chemistry, Jilin University, Changchun 130023, China

Correspondence should be addressed to Fu Honggang (email: yuht007@sina.com, fuhg@hlju.edu.cn)

Received September 18, 2001

Abstract The potential energy surface of HPO_2 system including eight isomers and twelve transition states is predicated at MP2/6-311++G(d, p) and QCISD(t)/6-311++G(3df,2p)(single-point) levels of theory. On the potential energy surface, *cis*-HOPO(E1) is found to be thermodynamically and kinetically most stable isomer followed by *trans*-HOPO(E2) and HPO(O)(C_{2v}, E3) at 10.99 and 48.36 kJ/mol higher, respectively. Based on the potential energy surface, only E1 and E3 are thermodynamically stable isomers, and should be experimentally observable. The products *cis*-HPOO(E5) and *trans*-HPOO(E6) in the first-step reaction of HP with O_2 can isomerize into isomer E1 that has higher stability. The reaction of OH with PO will directly lead to the formation of isomer E1. The computed results are well consistent with the previous experimental studies.

Keywords: potential energy surface, HPO_2 molecule, isomerization, stability.

The study on phosphorus and phosphorus-containing compounds is considerably interesting because they are very important in the area of combustion and material synthesis, and there are many experimental and theoretical studies of thiohydrides and oxyhydrides of phosphorus, and their many systems with hydrogen inclusion[1—3]. Some oxyhydrides of phosphorus and hydrogen-containing system have been characterized by means of microwave spectrum method, such as PO, PO_2, HPO, and H_2PO[4—7]. For homologous thiohydrides of phosphorus, the existent evidences and IR spectra were given for PS, P_2S, and PS_2 formed in electric discharge experiment of P_4 and S_8 mixtures by Mielke et al.[8]. Schenk and his coworkers[9] identified the existence of H_2PSH molecule in the electric discharge system of PH_3 and H_2S. In 1993, Mielke and his coworkers[10] firstly identified HPS_2 species by discharging the mixtures of PH_3 and S_8/Ar, and affirmed the structure to be *cis*-HPSS. But in our current theoretical study, we found that besides a small quantity of *cis*-HPSS, the products in the experiment were mostly a solid HP(SS) structure with PSS three-member ring. The HNS_2 and HPO_2, the analogs of HPS_2, have been experimentally and theoretically studied[11—15]. Because of very important role in the atmospheric chemistry, the HONO molecule has been carefully studied by Kleiner and his coworkers[16] by high-resolution spectroscopy. But there is no more available experimental and theoretical studies about HOPO radical, which is the analogy of HONO. Davies and his coworkers[11] identified the reaction step of OH with PO in the system of O and PH_3, and the product was predicated as HOPO radical. An experiment by Withnall et al.[12] showed that the product in the reaction of PH with O_2 was *cis*-HOPO rather than HPOO, indicating that there were isomerizations in the process. In 2000, the radical *cis*-HOPO has been detected in the gas phase for the first time using high resolution infrared laser absorption spectroscopy, and the experimental results were compared with the theoretical spectrum[14]. For exploring the isomer structures of HPO_2, isomerization, and the final products of reaction of PH with O_2 and OH with PO, we performed an *ab initio* MO computational study on the HPO_2 system. The computed results consist well with the experimental results, and show the reaction mechanism of PH with O_2 and OH with PO.

1 Computational methods

The equilibrium geometries, transition state, and molecular fragments were optimized using analytical gradient methods with second-order Moller-Plesset perturbation theory (MP2) and the split valence 6-311G basis set. In the paper, the structural parameters and zero-point vibrational energy were obtained at MP2/6-311++G(d, p) level of theory. The single-point energy of all stationary points was gained at QCISD(t)/6-311++G(3df,2p)//MP2/6-311++G(d, p) level of theory. QCISD(t) method is one of configuration interaction calculations and includes single and double substitutions with a triple contribution to the energy added. The energy at QCISD(t)/6-311++G(3df,2p)//MP2/6-311++G(d, p) level of theory was used on the potential energy surface and in all discussions of the paper. In order to confirm whether the obtained transition states connect the right reactants and products, the intrinsic reaction coordinate (IRC) calculations were carried out at the MP2/6-311++G(d, p) level of theory. All calculations have been carried out using the GAUSSIAN98 package running on the LEGEND/PIII800EB computer.

2 Results and discussion

2.1 Structures of isomers

The structures and geometry parameters of eight HPO_2 isomers computed at MP2/6-311++G(d, p) level of theory are shown in fig. 1, and their energy, zero-point energy, and relative energy are listed in table 1. The energy of isomer E1 *cis*-HOPO is the lowest at different levels of theory, and E1 is thermodynamically the most stable isomer followed by *trans*-HOPO(E2) at 10.99 kJ/mol higher. But for HPS_2 system, *trans*-HSPS is higher in energy than *cis*-HSPS, and the energy of *cis*-HNSS is the lowest in HNS_2 system. For isomers E1 and E2, the corresponding values of bond distances and bond angles are very near. The bond length between hydrogen-site oxygen atom and phosphorus atom is 0.163 nm, and the bond is a typical single bond. The bond length between the terminal oxygen atom and phosphorus atom is 0.148 nm, and the bond has a typical character of double bond. This result is similar to that found in the HPS_2 system. The next isomer is HPO(O) (E3), which has C_{2v} symmetry and $^1A_1$ electronic state. It is higher in energy than E1 by 48.36 kJ/mol, and the energy value shows that the isomer is possibly thermodynamically stable isomer. Similar structures also exist in HPS_2 and HNS_2 systems. But for HPS(S), the computed results show that it is thermodynamically and kinetically unstable isomer. Isomer E4 with C_s symmetry is a stereo structure involving POO three-member ring, and it is higher in energy than E1 by 426.53 kJ/mol. Succedent discussion shows that it is unstable, but similar structural isomer in HPS_2 was found to be higher thermodynamically and kinetically stable isomer. Isomers E5 and E6 are *cis*- and *trans*-HPOO, and their energy is higher than E1 by 582.32 and

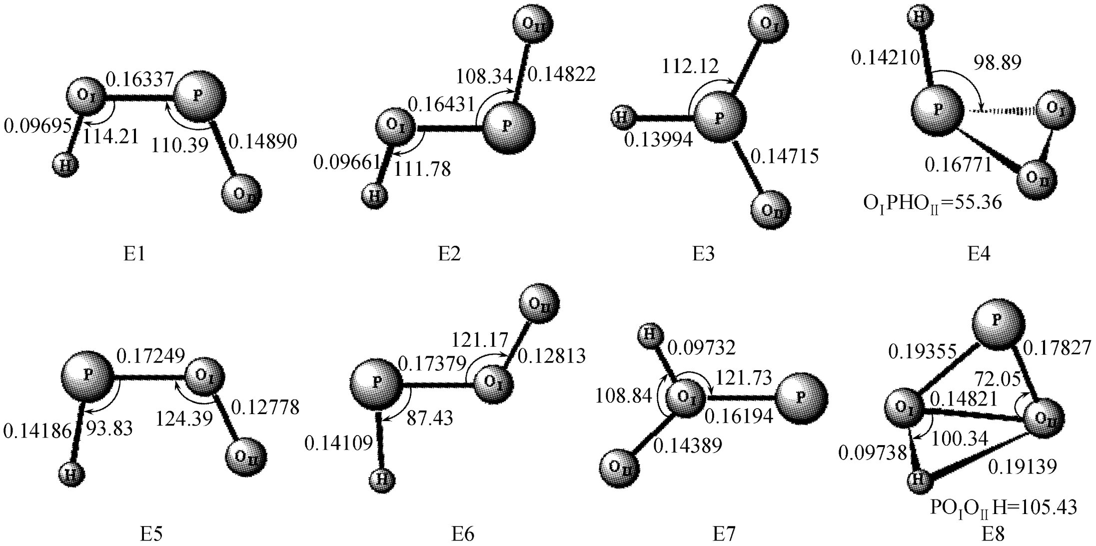

Fig. 1. Isomer structures of HPO_2 at MP2/6-311++G(d, p) level of theory. Bond distances are in nanometers, and bond angles in angle.

Table 1 Total energy (kJ • mol^{-1}), zero-point vibrational energy (kJ • mol^{-1}), and relative energy (kJ • mol^{-1}) of equilibrium geometries and transition states of HPO_2 system

Stationary points	MP2/ 6-311++G(d,p)	MP4SDQ/ 6-311++G(3df,2p)	QCISD(T)/ 6-311++G(3df,2p)	Zero-point vibrational energy	Relative energy
E1	−1290193.75	−1290570.85	−1290640.91	45.97	0.00
E2	−1290180.02	−1290559.48	−1290629.65	45.71	10.99
E3	−1290129.65	−1290516.65	−1290589.40	42.85	48.36
E4	−1289738.45	−1289947.65	−1290206.99	38.79	426.53
E5	−1289635.98	−1090128.90	−1290053.65	41.31	582.32
E6	−1289635.65	−1289946.48	−1290053.56	41.55	582.65
E7	−1289517.00	−1289907.15	−1289984.21	45.85	656.26
E8	−1289347.53	−1289743.92	−1289838.95	44.50	800.09
TS1/2	−1290154.10	−1290531.68	−1290602.02	41.57	34.39
TS2/3	−1289938.36	−1290305.15	−1290388.92	30.62	236.55
TS1/OH	−1289759.46	−1290060.29	−1290189.10	34.86	440.49
TS2/4	−1289688.89	−1290100.67	−1290145.62	38.57	487.68
TS3/4	−1289620.49	−1290004.98	−1290087.68	34.91	541.90
TS4/6	−1289530.73	−1289899.49	−1290016.65	34.78	612.79
TS4/5	−1289540.51	−1289901.82	−1290003.71	37.67	628.59
TS5/OH	−1289485.74	−1289857.02	−1289957.62	30.35	667.34
TS5/6	−1289511.90	−1289860.87	−1289956.24	35.51	673.90
TS2/7	−1289491.46	−1289881.08	−1289961.77	41.54	674.40
TS7/8	−1289316.69	−1289717.17	−1289804.80	42.17	831.90
TS6/8	−1289250.23	−1289630.30	−1289748.96	29.03	874.58

582.65 kJ/mol respectively. Subsequent computed results show that they are thermodynamically and kinetically unstable isomers. Other two isomers, E7 and E8, are too high in energy to exist stably. For HPS_2, there is an isomer of HSSP linked manner, but no HOOP isomers were found in HPO_2 system.

2.2 Stability and isomerization of isomers

The structures of computed twelve transition states of HPO_2 system are shown in fig. 2, and their total energy, zero-point energy, and relative energy are listed in table 1. The potential energy surface of HPO_2 is shown in fig. 3. Based on the potential energy surface shown in fig. 3, isomer E2 can isomerize into E1 via TS1/2 by a reaction barrier of 23.50 kJ/mol. Because E1 is the global point on the potential energy surface, it is thermodynamically the most stable isomer. Isomer E2 is unstable, and cannot be observed in experiments. There are two isomerizations for E3. One is from E3 to E2 via transition state TS2/3 by a barrier of 188.19 kJ/mol. Another process is from E3 to E4 via TS3/4 by a barrier of 495.54 kJ/mol. Because the two barriers are too high at thermochemical conditions to make the two isomerizations happen, E3 is stable isomer, and can be observed in experiments. The previous computed results showed that the similar structural radicals exist in HPS(S), HNO(O) and HNS(S), and they are stable isomers. Isomers E5 and E6 can isomerize into E4 via TS4/5 and TS4/6 by reaction barriers heights of 46.27 and 20.14 kJ/mol, respectively. And the isomerization from E4 to E2 can happen via a reaction barrier of 61.15 kJ/mol,

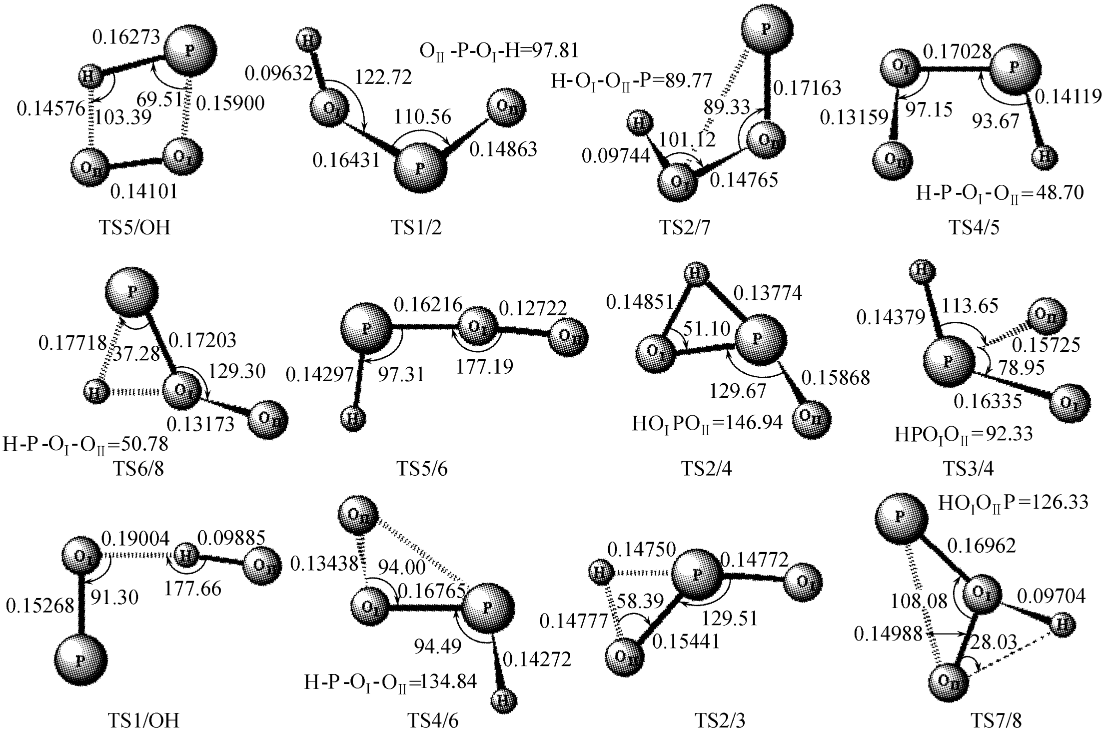

Fig. 2. Structures of transition state of HPO_2 system at MP2/6-311++G(d, p). Bond lengths are in nanometer, and bond angles in angle.

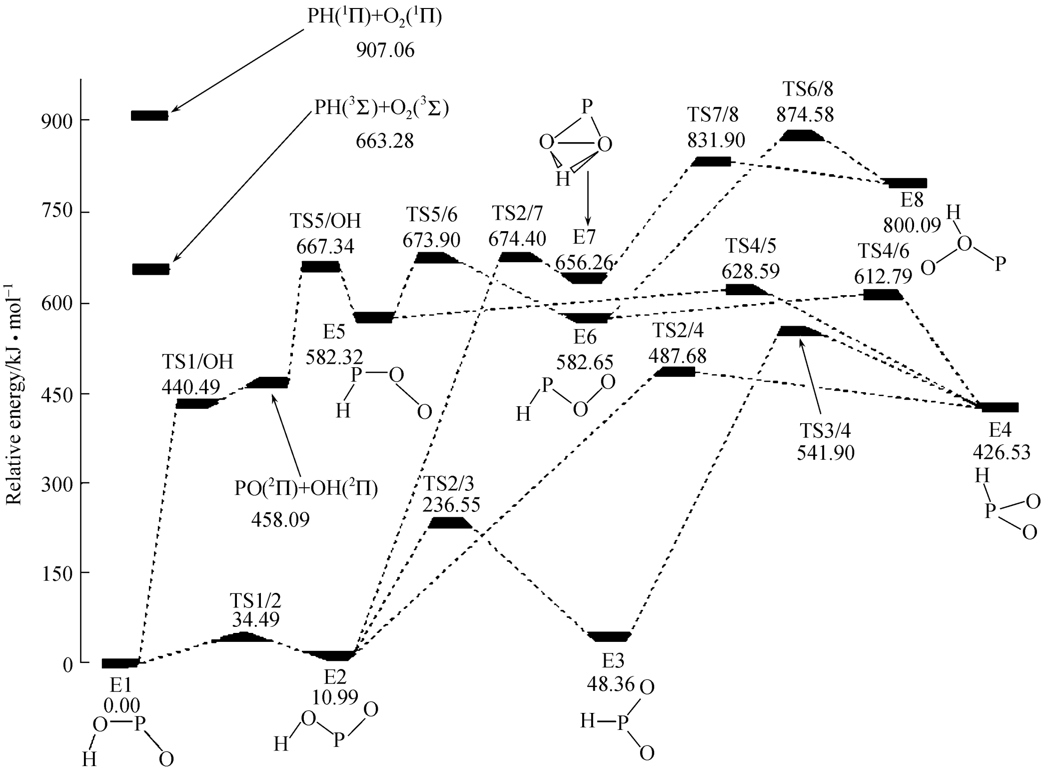

Fig. 3. Potential energy surface of HPO_2 system at QCISD(t)/6-311++G(3df,2p)//MP2/6-311++G(d,p) level of theory with zero-point vibrational energy inclusion.

and subsequent process is from E2 to E1. Therefore, isomers E4, E5 and E6 are unstable, and cannot be observed in experiments. The isomerization from E4 to E3 via TS3/4 needs a barrier of 115.37 kJ/mol, and the process will compete with another channel, from E4 to E2 via TS2/4. But TS2/4 is lower in energy than TS3/4 by 54.21 kJ/mol. Therefore the primary isomerization channel for E4 is from E4 to E2 via TS2/4, and subsequently, E2 changes to E1. The process that E8 changes to E7 by a 31.81 kJ/mol barrier height is followed by another process that E7 isomerizes into E2 via TS2/7 by a reaction barrier of 18.14 kJ/mol. Finally, E2 isomerizes into E1. Therefore, E7 and E8 are unstable. Based on the above discussion, for eight isomers of HPO_2 system, only *cis*-HOPO (E1) and HPO(O) (E3) are stable isomers, and should be observed in experiments.

2.3 Comparison with experiments

In all isomers of HPO_2 system, only E1 and E3 are stable isomers. There are many species that are similar in structure with E3, such as HPS(S), HBO(O), HNO(O), HNS(S), HAsO(O), and HSO(O). Heretofore, E3 has not been observed in experiments. Based on the above discussion, E3 is stable isomer. If appropriate reaction routes or precursors were selected, E3 should be observed in experimental spectrum. Davies and his coworkers gave the experimental evidences of existence of HOPO radical in 1968. They testified that the product of reaction of OH with OP is HOPO radical in the system of O and PH_3. On the potential energy surface shown in fig. 3, *cis*-HOPO can form in the reaction system of OH and PO via transition state TS1/OH. But it is surprising that transition state TS1/OH is lower in energy than PO and OH by 17.60 kJ/mol at QCISD(t)/6-311++G(3df,2p)//MP2/6-311++G(d,p) level of theory with zero-point vibrational energy inclusion. This instance also appears in the computational study of HPS_2 and HSO_2[17], and it shows that the reaction barrier of OH with OP closes to zero, or is a no-barrier reaction. In 1988, Withnall and his coworkers also observed the HOPO in the same reaction system to Davies, and investigated detailedly the IR spectrum of HOPO. Mielke deemed that the HOPO radical would form from PH in excess oxygen. Based on the potential energy surface shown in fig. 3, if *cis*-HPOO and *trans*-HPOO firstly form in the reaction of HP with O_2, they will isomerize into E4 via TS4/5 and TS4/6, which need reaction barrier of 46.27 and 23.50 kJ/mol, respectively. And next step, E4 will change to E2 by overshooting a 61.15 kJ/mol barrier height. Lastly, E2 isomerizes into E1 by a reaction barrier of 23.50 kJ/mol (Path I). In the all steps of Path I, the reaction barrier is so low that the isomerizations easily happen in the system of thermochemistry and electric discharge. Therefore, the formation of HOPO in the reaction of PH with O_2 is very easy, but there are several transition states and intermediates. In another path, *cis*-HPOO and *trans*-HPOO firstly form in the reaction of HP with O_2 followed by the isomerization from *trans*-HPOO to *cis*-HPOO, which needs 91.25 kJ/mol reaction barrier. The next step is the dissociation of *cis*-HPOO via TS5/OH that will lead to the formation of PO and OH, and lastly, the products of *cis*-HOPO forms from the reaction of PO with OH (Path II). Path II is lower in competitive ability than Path I. The first cause is that the reaction barrier heights are close to 84 kJ/mol in the isomerization from *cis*-HPOO to *trans*-HPOO and the dissociation of *cis*-HPOO via transition state TS5/OH. Another cause is that the secondary reaction of produced PO and OH need effective collision of two molecules, and if the concentration of reactants and collision probability are low, there is little possibility of reaction. Therefore, the primary channel of reaction of HP with O_2 in Mielke's experiment is Path I. In 2000, Bell identified the existence of *cis*-HOPO in the system including H_2, O_2, and P_4 by IR technology. There are two possible reaction mechanisms based on the potential energy surface (fig. 3). Because there are no available experimental data of the concentrations of OH and PH, we believe that if the concentrations of OH and PO are very high, the products will directly form. If the concentration of PH is higher, both Path II and Path I are possible reaction channels, because in the condition of photodecomposition, fragments can carry plentiful excess energy, which are higher than reaction barrier in Path II, and make reaction happen along Path II. But the reaction odd along Path I is higher than along Path II.

3 Conclusions

(i) Based on the potential energy surface of HPO_2 system, only *cis*-HOPO (E1) and HPO(O) which has C_{2v} symmetry and $^1A_1$ electronic state are stable isomers, and should be observed in experiment.

(ii) The isomers produced from the reaction of PH with O_2 will directly isomerize into E1 that is thermodynamically the most stable isomer.

(iii) The reaction of OH and PO will directly lead to the formation of *cis*-HOPO, and the barrier of reaction of OH with OP is close to zero.

Acknowledgements This work was supported by the National Natural Science Foundation of China (Grant Nos. 29892168, 20171015 and 20171016), Science Foundation for Excellent Youths of Heilongjiang University (2002), and the Natural Science Foundation of Heilongjiang Province (Grant No. E00-16).

References

1. Leung, Y. C., Wasser, J., Van Houten, S. et al., The crystal structure of P_4S_3, Acta Crystallogr., 1957,10: 574—582.
2. Griffin, A. M., Minshall, P. C., Sheldrick, G. M., Two new molecular phosphorous sulfides: α-P_4S_4 and β-P_4S_4; X-ray crystal structure of α-P_4S_4, J. Chem. Soc., Chem. Commun., 1976: 809—810.
3. Meisel, M., Grunze, H., New phosphorus sulfide phase P_4S_9, II. Different preparative methods, properties, and consitution of P_4S_9, Z. Anorg. Allg. Chem., 1970, 373: 265—278.
4. Kawaguchi, K., Saito, S., Hirota, E., Far-infrared laser magnetic resonance detection and microwave spectroscopy of the phophorus oxide (PO) radical, J. Chem. Phys., 1983, 79: 629—634.
5. Kawaguchi, K., Saito, S., Hirota, E., Far-infrared laser magnetic resonance detection and microwave spectroscopy of the PO_2 radical, J. Chem. Phys., 1985, 82: 4893—4902.
6. Saito, S., Endo, Y., Hirota, E., The microwave spectrum of an unstable molecule oxophosphine (HPO), J. Chem. Phys., 1986, 84: 1157—1159.
7. Hirao, E., Saito, S., Ozeki, H., Microwave spectrum and molecular structure of the dihydrophosphoryl rasical H_2PO in the $\tilde{X}^2A'$ ground electronic state, J. Chem. Phys., 1996, 105: 3450—3457.
8. Mielke, Z., Brabson, G., Andrews, L., Matrix infrared spectra of the phosphorus sulfides PS, P_2S, PS_2, J. Phys. Chem., 1991, 95: 75—79.
9. Schenk, P. W., Leutner, B., Existence of ternary compounds of phosphorus with sulfur and hydrogen, Angew Chem. Intern. Ed. Eng., 1966, 5: 898—900.
10. Mielke, Z., Andrews, L., Infrared spectra of $HSPH_2$, HPS_2, and $HSPS_2$ in solid argon, J. Phys. Chem., 1993, 97: 4313—4319.
11. Davies, P. B., Thrush, B. A., The reactions of atomic oxygen with phosphorus and with phosphine, Proc. Roy. Soc. A, 1968, 302: 243—252.
12. Withnall, R., Andrews, L., Infrared spectra of O-Atom-PH_3 reaction products trapped in solid argon, J. Phys. Chem., 1988, 92: 4610—4619.
13. Nakamura, S., Takahashi, M., Okazaki, R. et al., An *ab initio* MO study of isomers of HNS_2 and HNO_2, J. Am. Chem. Soc., 1987,109: 4142—4148.
14. Bell, I. S., Ahmad, I. K., Hamilton, P. A. et al., Detection of the transient molecule HOPO in the gas phase by infrared laser spectroscopy, Chem. Phys. Lett., 2000, 320: 311—315.
15. Lohr, L. L., Boehm, R. C., *Ab initio* study of the gaseous oxyacids of phosphorus, their conjugate bases, and their corresponding neutral radicals, J. Phys. Chem., 1987, 91: 3203—3207.
16. Kleiner, I., Guilmot, J. M., Carleer, M. et al., The ν_4 fundamental bands of *trans*- and *cis*-nitrous acid, J. Mol. Spectrosc., 1991, 149: 341—347.
17. Goumri, A., Rocha, J. -D. R., Laakso, D. et al., Characterization of reaction pathways on the potential energy surfaces for H + SO_2 and HS + O_2, J. Phys. Chem., 1999, 103: 11328—11335.