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Ab Initio Study of $PH_2 + O_2$ Reaction by Gaussian-2 Theory

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Ab initio calculations have been carried out for the $PH_2 + O_2$ reaction by using Gaussian-2 theory, which is considered a key reaction to understand low-temperature phosphine combustion. It has been suggested that the reaction proceeds through two main routes at low temperatures. One is the reaction to yield OH radicals, and the other yields hydrogen atoms. Of the two reactions, the latter seems to be the chain branching process, which enables the spontaneous ignition of phosphine at room temperature.

Introduction

Phosphine is used in the semiconductor industry as one of the major feedstock gases. One of the characteristic properties of phosphine is the spontaneous ignition at room temperature.[1] This phenomenon is particularly well-known for silane, which is a typical feedstock gas in advanced industries as well. The explosion phenomenon of phosphine was first explored by Shantarovich.[2] He has measured the temperature versus pressure relationship of the phosphine explosion and has identified the explosion peninsular for the phosphine−oxygen system, a similar one to what is well-known for the hydrogen−oxygen system. However, almost nothing has been done so far to make clear the combustion mechanism of phosphine. From a mechanistic point of view, the spontaneous ignition of gas in the air at room temperature is an extremely rare phenomenon. This is because there is very little possibility of encountering a chain branching process which occurs at room temperature in the gas phase.

In fact, quite a number of investigations have been made so far for silane combustion,[3−19] to identify the main reaction route which enables the spontaneous ignition.[14,18,19] For that purpose, it is crucial to investigate the elementary reactions which have relatively low activation energies and are active at low temperatures. Eventually, the reaction of silyl radical with oxygen molecule has been found to be the key to understanding the low-temperature silane combustion, of which the activation energy is zero[11] and the reaction rate is very fast even at room temperature.[7,8] In addition, a series of elementary reactions starting from this reaction have been concluded to make a chain branching process, yielding more than one active radical from only one radical of SiH_3.[18,19] Here, the fact that a possibility of a chain branching process has been found does suggest in itself that the process is the one responsible for the spontaneous ignition.

For phosphine combustion, therefore, it may be more than just worthwhile to investigate a similar reaction route. It is expected that the barrier height to the $PH_2 + O_2$ reaction is very low and a series of reactions which start from $PH_2 + O_2$ makes a chain branching process. To clarify the reaction mechanism, it will be of great help to carry out ab initio energetic calculations. The ab initio method is suitable to follow the reaction coordinates as well as to calculate the energetics of relevant molecules and radicals. As for the phosphine-related molecules, Howard and Platts have made ab initio calculations for some halogenated phosphines as well as for phosphine itself.[20] Antoniotti et al. have investigated gas-phase ion chemistry of phosphine.[21] On the other hand, Zachariah and Melius have made energetic calculations for various P−Si−H molecules.[22] However, almost nothing has been done for the P−O−H molecules so far except for some calculations of P_2O_2[23,24] and P_2H_4.[25]

The present paper reports on the detailed energetic calculations for various elementary reactions relevant to the $PH_2 + O_2$ reaction as well as for the related molecular species.

Results and Discussion

The objective of the present study is to construct a reliable energy diagram relevant to the $PH_2 + O_2$ reaction in order to find out the main reaction route for the low-temperature phosphine combustion. For the system of $SiH_3 + O_2$, which is the key reaction to understand the low-temperature silane combustion, a similar diagram was first constructed by Darling and Schlegel,[11] of which the main reaction route was later revised by Koshi et al.[14] and further revised by the present authors.[18,19] Most of the molecules and radicals appearing in the silane diagram have only one Si atom in each of them, and we may be able to make a similar diagram for the $PH_2 + O_2$ system by substituting P atom for each Si atom and reducing the number of H atoms by one. For example, molecules such as SiH_3O, H_2SiOOH, *c*-$OSiH_2O$, and so on may find their counterparts in PH_2O, HPOOH, *c*-OPHO, and so forth, respectively. In this way, the major radicals and reaction routes connecting between them can be listed up to carry out detailed ab initio calculations. All the calculations have been carried out by the Gaussian-94 program[26] on a Cray computer or on an IBM computer. The energetic calculations have been made by Gaussian-2 theory.[27]

At first, calculations have been done to obtain the optimized structures of various molecules and radicals by the HF/6-31G*

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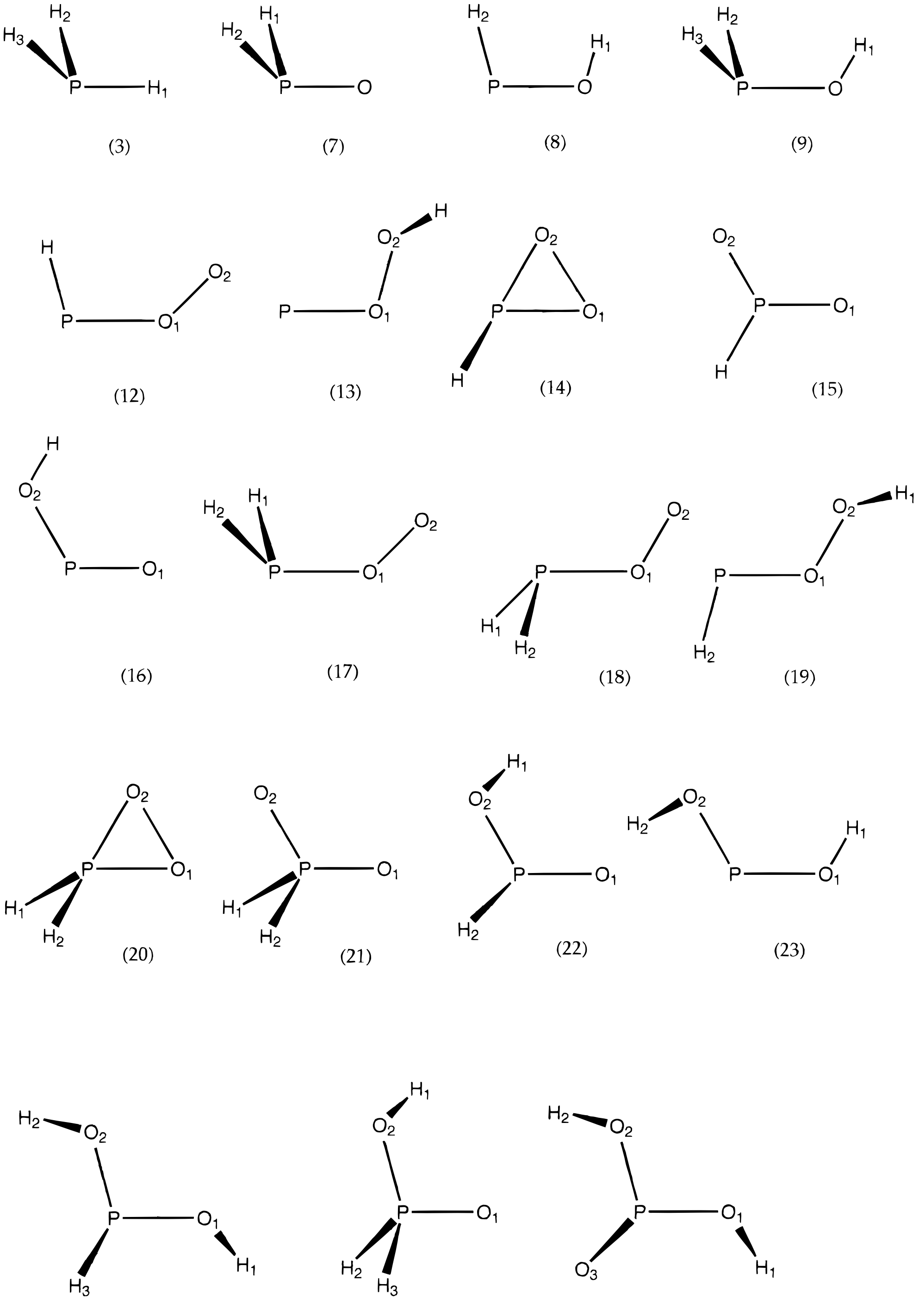

Figure 1. Geometrical conformations and atomic numbering for the molecules and radicals relevant to the $PH_2 + O_2$ reaction route.

method. The geometry optimizations have also been made by the MP2=FULL/6-31G* method. The calculations have been made for 26 molecules in total. The obtained values of molecular parameters are summarized in Table 1S of the Supporting Information. Figure 1 shows the numberings of atoms in larger molecules. The Gaussian-2 energy values have been obtained according to the procedure defined by Pople et al.[27] and are listed in Table 1. The zero-point and thermal energy corrections at 298 K listed in Table 1 have been calculated based on the HF/6-31G* frequencies multiplied by a factor of 0.893. For *c*-OPH_2O, however, since the molecular parameters and frequencies obtained with the HF/6-31G* method are very different from those obtained with the MP2=FULL/6-31G*, the zero-point and thermal energy corrections have been made based on the MP2=FULL/6-31G* frequencies multiplied by a factor of 0.927.

As stated, it is expected that $PH_2O + O$ in the $PH_2 + O_2$ system resembles $SiH_3O + O$ in the $SiH_3 + O_2$ system, and HPOOH resembles H_2SiOOH. This has been confirmed to be true from the energetic calculation. However, the energy of *c*-OPHO + H relative to that of $PH_2 + O_2$ has been found to be much higher than that of *c*-$OSiH_2O$ + H relative to $SiH_3 + O_2$. Actually, the energy of *c*-OPHO + H is 9.61 kcal/mol higher than that of $PH_2 + O_2$, while that of *c*-$OSiH_2O$ + H is 25.49 kcal/mol lower than that of $SiH_3 + O_2$.[18] Rather, the energy of

TABLE 1: Energies of Molecules and Radicals

	energies (in au)				
molecules and radicals	MP2=FULL/6-31G(d)	G-1 (0 K)	G-2 (0 K)	ZPE (kcal/mol)	thermal (kcal/mol)
(1) PH (triplet)	−341.343 848	−341.427 356	−341.428 435	3.27	1.48
(2) PH_2	−341.945 789	−342.047 251	−342.049 134	8.19	1.79
(3) PH_3	−342.562 259	−342.676 528	−342.679 021	14.67	1.83
(4) PO	−415.838 058	−416.024 881	−416.020 982	1.79	1.49
(5) HPO	−416.427 715	−416.628 006	−416.628 786	6.28	1.81
(6) POH	−416.369 208	−416.572 516	−416.572 955	7.96	1.83
(7) PH_2O	−416.985 896	−417.194 224	−417.201 549	11.55	1.99
(8) HPOH (cis)	−416.999 772	−417.208 402	−417.310 690	12.66	2.25
(9) H_2POH (cage)	−417.609 642	−417.829 956	−417.832 912	19.23	2.11
(10) OPO	−490.905 733	−491.194 620	−491.195 965	3.39	2.08
(11) POO	−490.703 415	−490.999 801	−490.997 938	3.04	2.10
(12) HPOO (cis)	−491.329 525	−491.627 952	−491.627 810	7.80	2.49
(13) POOH (triplet)	−491.338 682	−491.632 266	−491.632 210	10.32	2.49
(14) *c*-OPHO	−491.378 070	−491.681 930	−491.681 455	9.25	2.02
(15) *w*-OPHO	−491.519 785	−491.820 477	−491.823 175	10.40	2.04
(16) OPOH	−491.540 371	−491.841 182	−491.842 488	10.88	2.17
(17) H_2POO (cage)	−491.911 652	−492.229 338	−492.230 346	14.29	2.51
(18) H_2POO (C_1-type)	−491.911 511	−492.229 350	−492.230 565	14.04	2.71
(19) HPOO	−491.940 814	−492.249 699	−492.250 726	15.58	2.75
(20) *c*-OPH_2O[a]	−491.902 153	−492.214 738	−492.217 043	16.54	2.42
(21) *w*-OPH_2O	−492.013 768	−492.329 239	−492.332 850	15.23	2.34
(22) OPHOH	−492.068 915	−492.381 586	−492.385 104	16.13	2.50
(23) HOPOH	−492.073 303	−492.387 477	−492.389 716	16.16	2.63
(24) HOPHOH	−492.683 006	−493.006 242	−493.010 129	23.40	2.70
(25) OPH_2OH	−492.696 268	−493.018 532	−493.023 322	22.90	2.68
(26) $OP(OH)_2$	−567.148 495	−567.566 257	−567.570 821	19.51	3.32

[a] Zero-point and thermal energy corrections were made based on the frequencies obtained with the MP2=FULL/6-31G* method multiplied by 0.927.

TABLE 2: Energies of Transition States

	energies (in au)				
reaction	MP2=FULL/6-31G(d)	G-1 (0 K)	G-2 (0 K)	ZPE (kcal/mol)	thermal (kcal/mol)
(1) $PH_2 + O_2 = H_2POO$ (cage)[a]	−491.872 097	−492.201 333	−492.202 283	12.39	2.78
(2) H_2POO (cage) = $PH_2O + O$	−491.811 140	−492.174 416	−492.175 629	12.63	2.54
(3) $PH_2O = HPOH$	−416.904 681	−417.132 316	−417.133 955	9.39	1.91
(4) H_2POO (cage) = HPOOH	−491.860 690	−492.192 300	−492.192 311	11.72	2.28
(5) HPOOH = HPO + OH	−491.891 888	−492.239 537	−492.240 654	13.55	2.87
(6) HPO = POH	−416.317 257	−416.525 247	−416.525 194	4.41	1.80
(7) H_2POO (cage) = *c*-OPH_2O[a]	−491.873 534	−492.197 702	−492.198 609	13.85	2.46
(8) *c*-OPH_2O = *w*-OPH_2O[a]	−491.846 381	−492.209 943	−492.212 102	12.91	2.28
(9) *w*-OPH_2O = OPHO + H	−491.990 774	−492.321 608	−492.326 152	11.38	2.42
(10) OPHO = OPOH	−491.442 132	−491.747 698	−491.761 004	8.73	2.44
(11) *w*-OPH_2O = OPHOH	−491.983 921	−492.312 424	−492.316 359	13.08	2.21
(12) OPHOH = OPOH + H	−492.029 075	−492.343 240	−492.345 390	11.37	2.89
(13) OPHOH = HOPOH	−491.994 756	−492.325 429	−492.327 956	13.45	2.44
(14) HOPOH = PO + H_2O	−492.021 375	−492.333 294	−492.334 991	14.73	2.22
(15) HOPOH = OPOH + H	−491.994 767	−492.323 789	−492.325 608	11.36	2.66

[a] Zero-point and thermal energy corrections were made based on the frequencies obtained with MP2=FULL/6-31G* method multiplied by 0.927.

c-OPH_2O relative to $PH_2 + O_2$ is similar to the energy of *c*-$OSiH_2O$ + H relative to $SiH_3 + O_2$.

Then, for each combination of reactants and products, calculation has been carried out to find out a saddle point on the potential surface. The geometrical parameters for the transition states thus obtained with the MP2=FULL/6-31G* method are listed in Table 2S of the Supporting Information, where the numbering of atoms are illustrated in Figure 2. The energy values of the transition states have been obtained by Gaussian-2 theory. The zero-point and thermal corrections to the energies at 298 K listed in the table have been obtained based on the HF/6-31G* frequencies multiplied by a factor of 0.893. For the cases in which the transition state geometry obtained with the HF/6-31G* method is extremely different from that obtained with the MP2=FULL/6-31G* method, the corrections have been made based on the MP2=FULL/6-31G* frequencies multiplied by a factor of 0.927. The results are summarized in Table 2.

Figure 3 shows the energy diagram for the $PH_2 + O_2$ system at 298 K. The barrier height to the initial process from $PH_2 + O_2$ to H_2POO has been found to be zero. In the diagram, there are various kinds of decomposition and isomerization reactions. Among others, transfer of a hydrogen atom between adjacent atoms in a molecule is one of the typical isomerization reactions, e.g., the barrier height to the reaction from PH_2O to HPOH is 42.34 kcal/mol.

1. Reaction Route to Yield Oxygen Atoms. In the case of silane combustion, the reaction route of $SiH_3 + O_2 \rightarrow SiH_3OO \rightarrow SiH_3O + O$ was at first considered to be a chain-branching process responsible for the spontaneous ignition, because oxygen atoms can readily react with SiH_4 to yield two active radicals of SiH_3 and OH at room temperature.[5] However, soon it has

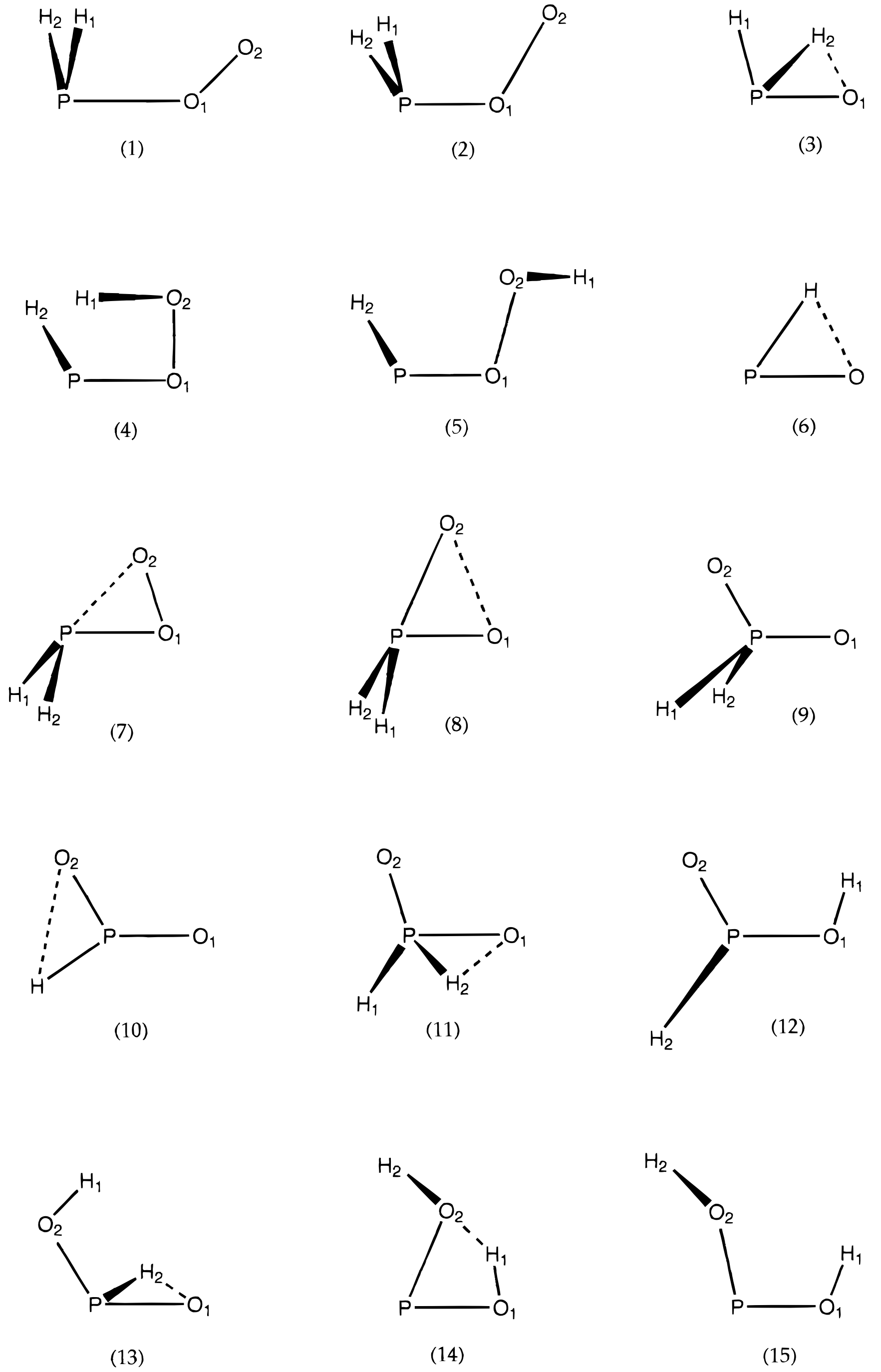

Figure 2. Geometrical conformations and atomic numbering for the transition states relevant to $PH_2 + O_2$ reaction route.

been found that the energy of SiH_3O + O is 10.99 kcal/mol higher than the original reactants of $SiH_3 + O_2$.[11] It is obvious that the energy barrier of this magnitude does not allow the reaction to be active enough at room temperature. As is seen in Figure 3, the present situation for the oxygen atom producing reaction is very similar to that of silane. The transition state from H_2POO to PH_2O + O is 34.10 kcal/mol higher than H_2POO, which means that the transition state is 12.63 kcal/mol higher than the original reactants of $PH_2 + O_2$. The energy of PH_2O + O itself is 8.24 kcal/mol higher than $PH_2 + O_2$. Thus, it has become clear that the reaction cannot be the chain-branching process for the spontaneous ignition.

2. Reaction Route to Yield OH Radicals. H_2POO molecules resulting from $PH_2 + O_2$ may be in the excited vibrational states and may readily undergo subsequent reactions. Figure 3 shows that the subsequent process may occur in two different ways. One is the hydrogen migration to yield HPOOH, of which the barrier (TS_1) is 23.63 kcal/mol. This means that TS_1 is only 2.16 kcal/mol higher than the original reactants of $PH_2 + O_2$ and may proceed with a favorable rate at room temperature. The resulting HPOOH may further undergo self-decomposition to yield HPO + OH. This reaction route is similar to the one for silane; $SiH_3 + O_2 \rightarrow SiH_3OO \rightarrow H_2SiOOH \rightarrow SiH_2O + OH$. The transition state energy from SiH_3OO to H_2SiOOH is 17.5 kcal/mol lower than the original reactants of $SiH_3 + O_2$.[11]

3. Reaction Route to Yield Hydrogen Atoms. Figure 3 shows that another reaction route of H_2POO is isomerization to yield *c*-OPH_2O. In this reaction, the oxygen atom at the end of H_2POO molecule is brought to the phosphorus atom at the top to form a cyclic structure. The barrier height to this reaction

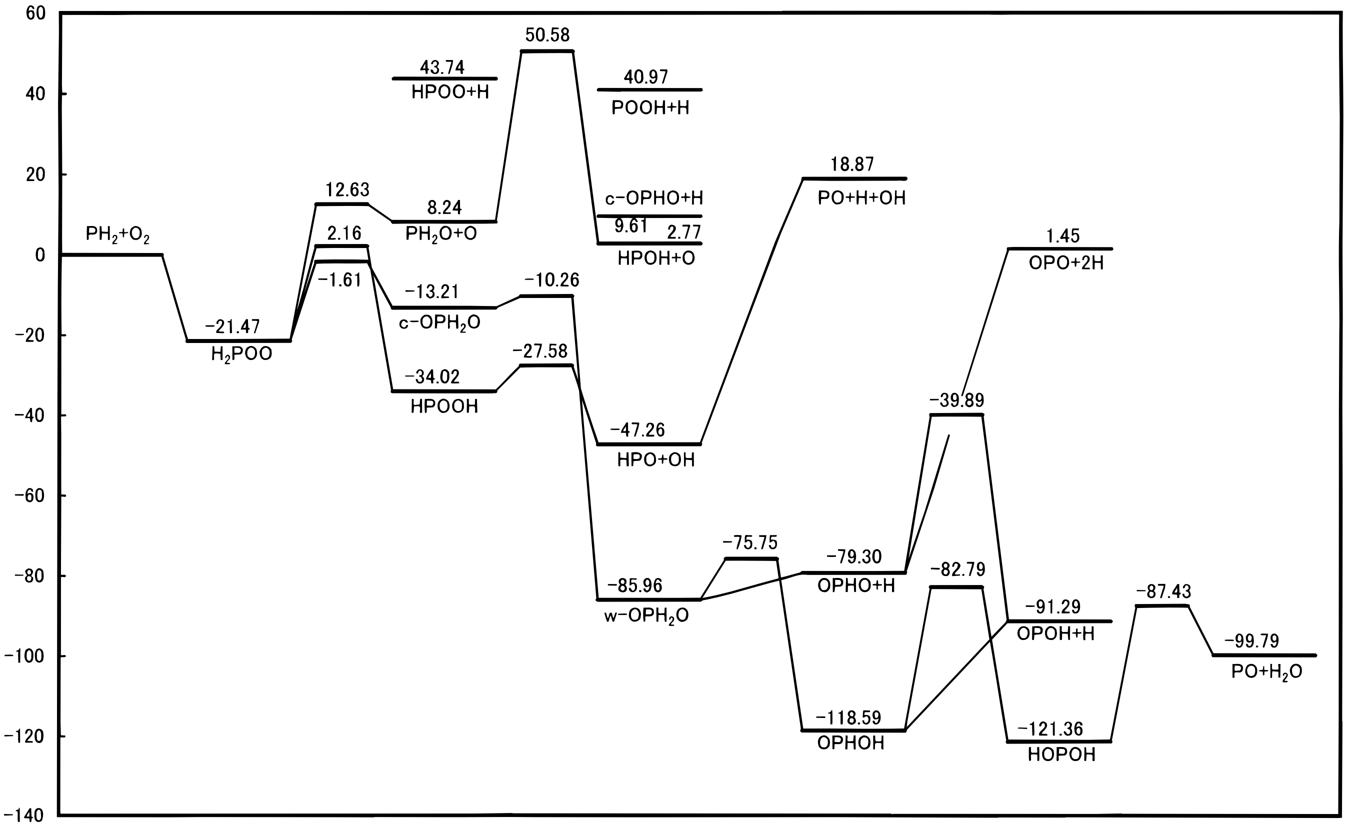

Figure 3. Energy diagram for the $PH_2 + O_2$ reaction route calculated at the level of Gaussian-2 theory.

is 19.86 kcal/mol, which means that the energy of the transition state (TS_2) is 1.61 kcal/mol lower than the original reactants. This reaction is similar to the one for silane, SiH_3OO = *c*-$OSiH_2O$ + H,[14,18] but is different in that the latter reaction releases a hydrogen atom whereas the former does not. *c*-OPH_2O further undergoes isomerization to yield *w*-OPH_2O. The barrier height to this reaction is only 2.95 kcal/mol. The *w*-OPH_2O molecule may find its counterpart in the *w*-$OSiH_2O$ molecule in the silane combustion system. The *w*-$OSiH_2O$ molecule has a biradical character, and the two SiO bonds are considered to be single bonds rather than double bonds.[19] A similar thing is expected in *w*-OPH_2O as well. Comparison between the energies of the reactant and product indicates that the increase of the OPO angle much stabilizes the molecule and that the resulting *w*-OPH_2O molecule is expected to have a large amount of excess energy.

This isomerization process is very interesting, because it has been found that both the reactant and product molecules have C_s symmetry and their ground electronic states belong to 2-A′ and 2-A″ symmetry, respectively. In other words, the electronic state of *c*-OPH_2O molecule is symmetric to the mirror plane of the molecule, whereas that of *w*-OPH_2O is antisymmetric. It is obvious that if the C_s symmetry is maintained during the course of this isomerization reaction, it is impossible for the molecule to go from A′ to A″ symmetry by this reaction. In this relevance, it is to be noted that the transition state (TS_3) of this reaction is very much out of symmetry; the two P−H bonds are much different from each other both in bond lengths and bond angles. The reaction may have been made possible through mixing of different electronic states, which was enabled by the collapse of the mirror symmetry during the reaction.

w-OPH_2O may further undergo isomerization to yield OPHOH, which still more stabilizes the molecule. The barrier height to this reaction is 10.21 kcal/mol. The latter molecule can further be converted to HOPOH, where the barrier height is 35.80 kcal/mol. These reactions correspond to the one from *w*-$OSiH_2O$ to OSiHOH[19] and the one from OSiHOH to HOSiOH[11,18] in silane oxidation, respectively. The corresponding barrier heights are also much the same for both systems. The barrier height to the decomposition reaction of HOPOH to yield PO + H_2O is 33.93 kcal/mol. The structure of the transition state of this reaction is also very much like the one for the reaction from HOSiOH to SiO + H_2O.[18]

4. Chain Branching Process for the Spontaneous Ignition. It is remarkable that the barrier to the decomposition reaction of *w*-OPH_2O into OPHO + H is only 6.66 kcal/mol, which is just the energy difference for the reaction. The barrier to the isomerization reaction from OPHO to OPOH is 39.41 kcal/mol. On the other hand, the barrier height to the decomposition reaction of OPHO to yield OPO + H is just the energy difference, though the value is as much as 80.75 kcal/mol in this case.

It should be noted here that the energy of OPO + 2H as a product of the $PH_2 + O_2$ reaction is only 1.45 kcal/mol higher than the energy of the reactants. The whole reaction route is summarized as follows:

$$PH_2 + O_2 \rightarrow H_2POO \rightarrow c\text{-}OPH_2O \rightarrow w\text{-}OPH_2O \rightarrow OPHO + H \rightarrow OPO + 2H$$

The barrier height of 1.45 kcal/mol may be easily overcome to obtain a favorable reaction rate even at room temperature. At least a certain portion of the products of the $PH_2 + O_2$ reaction may reach OPO + 2H to increase the number of active carriers and this may be considered the cause of the spontaneous ignition of phosphine at room temperature. This process is very much like the one for the silane case,

$$SiH_3 + O_2 \rightarrow SiH_3OO \rightarrow c\text{-}OSiH_2O + H \rightarrow w\text{-}OSiH_2O + H \rightarrow OSiHOH + H \rightarrow OSiOH + 2H$$

This reaction route produces two hydrogen atoms from one SiH_3 to make a chain-branching process for the spontaneous ignition of silane.[19]

Conclusion

The energy diagram has been calculated for the $PH_2 + O_2$ reaction by using Gaussian-2 theory. At low temperatures, this reaction may proceed through two main reaction routes. One is the reaction to yield OH radicals, and the other yields hydrogen atoms. Of the two reaction routes, the former produces one OH radical from one PH_2 and may just maintain the active chain. On the other hand, the latter is composed of a long reaction pathway of

$$PH_2 + O_2 \rightarrow H_2POO \rightarrow c\text{-}OPH_2O \rightarrow w\text{-}OPH_2O \rightarrow OPHO + H \rightarrow OPO + 2H$$

to eventually yield two hydrogen atoms from one PH_2 radical. It is possible that this reaction route is the one responsible for the spontaneous ignition of phosphine in the air at room temperature.

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Supporting Information Available: Tables 1s and 2s giving the molecular parameters and the geometrical parameters of the transition states obtained with the MP2=FULL/6-31G* method. This material is available free of charge via the Internet at http://pubs.acs.org.

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