

Theoretical Study of the Reaction $\text{PH}_5 \rightarrow \text{PH}_3 + \text{H}_2$

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Abstract: It is first pointed out that the pseudorotation and turnstile processes for the isomerization of PH_5 are topologically equivalent and that while pseudorotation goes through a valley of the potential energy surface, turnstile proceeds on the slope of the same valley with no stationary properties of the "turnstile transition state". The potential energy surface (PSE) for the reaction $\text{PH}_5 \rightarrow \text{PH}_3 + \text{H}_2$ is first discussed qualitatively, then in terms of ab initio calculations in C_{2v} and finally in C_s symmetry. The results are very sensitive to the level of computational sophistication. On an intermediate level (SCF with polarization functions) two saddle points are found, one of which corresponds to a Woodward-Hoffmann (WH)-allowed concerted reaction and the other to a non-least-motion variant of a WH-forbidden process that is better described as a zwitterionic reaction going via $\text{PH}_4^+ + \text{H}^-$. The barrier for the concerted process is slightly smaller than that for the zwitterionic one, but the region of the PES between the two "saddle points" is extremely flat. The transition state is especially nonrigid and there is no clear-cut distinction between two "reaction channels". On a higher level of sophistication (with inclusion of electron correlation) only the "concerted" saddle point "survives", but the saddle point region remains very flat. The best value for the barrier height is 36 kcal/mol (above PH_5) such that PH_5 should, in spite of the exoergicity of the reaction $\text{PH}_5 \rightarrow \text{PH}_3 + \text{H}_2$ (-38 kcal/mol), be metastable as an isolated molecule. Catalytic amounts of acids (even another PH_5 molecule may serve as a Lewis acid) are expected to lower the barrier for the decomposition of PH_5 considerably.

I. Introduction

The molecule PH_5 is interesting from various points of view.

(1) PH_5 is the prototype of the phosphoranes PR_5 . The special features of binding in compounds of pentavalent phosphorus, concerning, e.g., the possible description via a three-center, four-electron bond and the importance of d AO contributions,^{1,2} should show up in nuce.

(2) PH_5 is even one of the simplest of all electron-rich molecules.

(3) PH_5 is a typical and one of the simplest "nonrigid" molecules. Its isomerization barrier (from the D_{3h} ground configuration via a C_{4v} structure) is only ~ 2 kcal/mol.^{3,4} This is in obvious contrast to the rigidity of PH_3 , which has an inversion barrier of ~ 38 kcal/mol.⁵

(4) PH_5 has not yet been observed experimentally. The question why this is so is challenging. There is no doubt³ that the trigonal-bipyramidal D_{3h} structure represents a local minimum of the potential hypersurface. However, this minimum is ~ 38 kcal/mol above the energy of separated $\text{PH}_3 + \text{H}_2$.³ Hence PH_5 is at best metastable and the question of how high the barrier for its deintegration is becomes crucial. Its determination will be one of the main aims of this paper.

(5) The results of quantum-chemical calculations of PH_5 are extremely sensitive to the choice of the orbital basis, mainly the inclusion of d AOs (and even their exponent³) and the inclusion of electron correlation. The potential hypersurface for the reaction $\text{PH}_5 \rightarrow \text{PH}_3 + \text{H}_2$ changes dramatically on going from an SCF calculation without polarization functions via an SCF calculation with a good basis to a calculation in which electron correlation is taken into account. This will be demonstrated in this paper.

(6) The concerted ee (equatorial equatorial) H_2 abstraction is WH (Woodward-Hoffmann) allowed⁶ and has nevertheless a high barrier. A non-least-motion variant of the WH-forbidden ea (equatorial axial) abstraction, which leads via an ion pair $\text{PH}_4^+ - \text{H}^-$, is energetically almost competitive although it is, at variance with the result of an earlier calculation,⁷ not the lowest-energy path.

The equilibrium structure and the force field of PH_5 (as well as its harmonic vibration frequencies) have been published recently together with a reliable value for the inversion barrier. Since the discussion is still going on⁴ as to whether the turnstile mechanism for isomerization proposed by Ugi⁸ is competitive with Berry's pseudorotation,⁹ we have also taken up this point, which we shall treat in section III after a short presentation of methods and basis

sets in section II. Sections IV-VI contain the main topic, namely the potential hypersurface for the reaction $\text{PH}_5 \rightarrow \text{PH}_3 + \text{H}_2$, after a general discussion is given (section IV), first under C_{2v} constraint (section V) and then in C_s symmetry (section VI).

II. Method and Basis Sets

The computations on which this report is based were mainly of the ab initio SCF type in a basis set of Gaussian lobe functions. For some selected points electron correlation was taken care of by the CEPA method¹⁰ which is a size-consistent variant of the conventional configuration interaction method (for a recent review of the theory see ref 11). The computer programs used are described in ref 12 and 13.

The standard basis set consisted of a Huzinaga¹⁴ (10s/6p) basis in the contraction (4,6 \times 1/3,3 \times 1) augmented by a d set with $\eta = 0.925$ for P and a Huzinaga 4s basis in the contraction (3,1) augmented by a p set with $\eta = 0.65$ for H. In the calculations with correlation the d exponent of P was chosen as $\eta = 0.57$. In some test calculations, mainly in the "zwitterionic region", "flat" basis functions were added but found to have no significant effect.

A basis without polarization functions (d on P and p on H) was used for comparison.

Three levels of computational sophistication are referred to as A, B, and C in the text—namely (A) SCF without polarization functions, (B) SCF with polarization functions, and (C) CEPA

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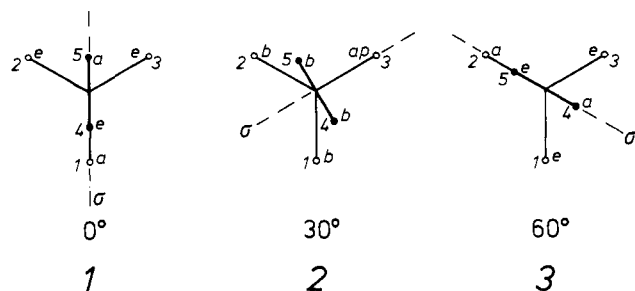


Figure 1. Illustration of the equivalence of the pseudorotation and turnstile isomerizations. e and a refer to equatorial and axial in the D_{3h} structure, b and ap to basal and apical in the C_{4v} structure. Open circles characterize the pyramidal and closed circles the trigonal subunits in the turnstile process. 1, 2, and 3 are starting, transition, and final structures. The essential symmetry plane for any of these structures is σ .

with polarization functions. The contour line diagrams of the potential surfaces given here are based on level B.

III. The Inversion Barrier. Turnstile vs. Pseudorotation

PH_5 in its equilibrium configuration has three equatorial (e) and two axial (a) bonds.

In the pseudorotation proposed by Berry⁹ one of the e bonds becomes apical (ap) in the tetragonal pyramidal C_{4v} form, while the other e and the two a bonds become basal (b). Then the two e and the two a bonds exchange their role, such that the process is of the (eaa) \rightleftharpoons (aee) type.

The turnstile rotation of Ugi⁸ consists formally of the following three steps: (1) a deformation of the D_{3h} molecule such that three H atoms (eea) form with P a regular trigonal pyramid, the C_3 axis of which coincides with the C_2 axis of the equilateral triangle formed by P and the other two H atoms (ea), (2) a torsion of the two subunits by 60° such that an arrangement equivalent to that at the end of step 1 is obtained, and (3) step 1 taken in the reverse order. The saddle point corresponds to a torsion of 30° in step 2.

The turnstile rotation is illustrated schematically in Figure 1.

The configuration reached at the end of step 1 is well-defined as the energetic minimum with respect to two PH distances and two HPH angles (in the triangular and the pyramidal subsystems). The energy of this configuration is found to lie 8.8 kcal/mol above the equilibrium configuration (CEPA value; in SCF one gets 10.3; values reported in ref 4 are in fair agreement with ours). The barrier for the second step (the "pure turnstile" rotation) is only 0.3 kcal/mol, such that the turnstile transition state is 9.1 kcal/mol above the ground configuration and ~ 7 kcal/mol above the Berry transition state.

One can now argue⁴ that by relaxation of the geometry, e.g., not requiring coinciding axes for the subunits, or by relaxation of the symmetry of the subunits, one is able to lower the turnstile barrier such that it may become competitive with the Berry barrier. Shih et al.⁴ have investigated such a geometry relaxation without arriving at a definite conclusion.

However, if one looks carefully enough at Figure 1 one realizes that the pseudorotation and the turnstile processes are topologically equivalent.¹⁵ Both are of the (eaa) \rightleftharpoons (aee) type. One can, in fact, regard Figure 1 also as an illustration of the Berry process, looked at from a somewhat unconventional perspective. The starting and the end point have C_s symmetry with three H atoms in the symmetry plane; the transition point has C_s structure with only one H atom in the symmetry plane. The lowest-energy structures of these symmetries happen to have the higher symmetries D_{3h} , C_{4v} , and D_{3h} . If one optimizes the turnstile process by full geometry relaxation it collapses to the Berry process.

We have computed various structures between the Berry and the turnstile "transition states" just by interpolating all geometrical parameters and got the curve in Figure 2, which clearly indicates that the "turnstile transition state" is no transition state at all since

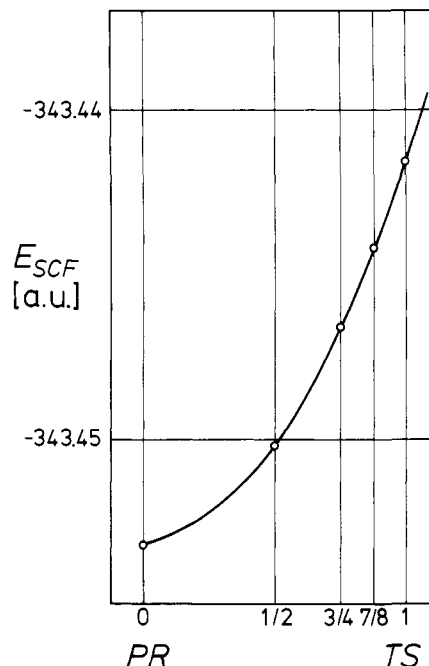


Figure 2. Energies for geometries interpolated between the pseudorotation (PR) and the turnstile (TS) transition states (level B).

it has no stationary properties (except the artificial ones in terms of which it is defined) and it lies on the slope of a valley, the bottom of which is given by a pseudorotation path.

IV. General Remarks of the PES for the Reaction $\text{PH}_5 \rightarrow \text{PH}_3 + \text{H}_2$

A priori there are three possibilities for a concerted H_2 abstraction from PH_5 (in its D_{3h} structure)—(aa) two axial H atoms removed, (ee) two equatorial H atoms removed, and (ae) one equatorial and one axial H removed.

The "least motion" path is (ae). It is WH forbidden,⁶ not strictly by symmetry, but by approximate local symmetry. From the two localized (a and e) MOs of the PH bonds in PH_5 one can construct two linear combinations, one approximately symmetric, the other approximately antisymmetric with respect to the bisecting plane, while the MO of both the abstracted H_2 and the lone pair of PH_3 are symmetric with respect to this plane. Since the two PH bonds (one a, one e) are different, there is not even a strict local symmetry and the WH argument is not fully convincing. However, if one studies this least-motion path by an ab initio calculation one finds that initial ground state and final ground state correspond to different electronic configurations and that the energies of these configurations cross at an energy ~ 200 kcal/mol above that of PH_5 . By using a two-configuration wave function the crossing can be "avoided" and a barrier below this crossing obtained, but even then the barrier would be much higher than that on the "allowed" path. So the WH argument is confirmed.

The (ee) and (aa) abstraction need not be regarded as independent processes. In the (aa) abstraction one must first bring the two axial atoms closer together; this is easily achieved by a pseudorotation. The (ae) abstraction is then supposed to follow the same way as the (ee) abstraction. For the same reason the "diagonal" abstraction of two opposite basal or of one basal and one apical H atom from the square-pyramidal form (the transition state of pseudorotation) need not be considered separately, while the abstraction of two neighboring basal atoms corresponds to the (ae) abstraction from the D_{3h} configuration.

Howell⁷ went one step further and claimed that even the (ee) and the (ae) abstraction follow the same path.

He selected two internal coordinates, namely the H-H distance r in the leaving H_2 and the distance \bar{R} between P and the midpoint of the leaving H_2 (this \bar{R} is different from what we shall call R). For a two-dimensional grid of (\bar{R} , r) values the energy was op-

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Table I. Computed Total Energies in Hartrees (1 hartree = -627.5 kcal/mol)

molecule	geometry ^a	level A	level B	level C
		(SCF without polarization functions)	(SCF with polarization functions) $\eta_d = 0.925$	(CEPA with polarization functions) $\eta_d = 0.57$
PH_5	$D_{3h}, r_{\text{ax}} = 2.77, r_{\text{eq}} = 2.665$	-343.32732	-343.45820	-343.65667
PH_5	$D_{3h}, r_{\text{ax}} = r_{\text{eq}} = 2.685$		-343.45709	-343.65612
PH_4	$C_{2v}, r_1 = r_2 = 2.96, r_3 = r_4 = 2.69$ $\alpha_{12} = 172^\circ, \alpha_{34} = 97^\circ$		-342.61380	
PH_4^+	$T_d, r = 2.60$		-342.71865	-343.86682
PH_4^+	$T_d, r = 2.70$		-342.71363	
PH_3	$C_{3v}, r = 2.677, \alpha = 92.5^\circ$	-342.33384	-342.39706	-343.55507
PH_3	$C_{3v}, r = 2.685, \alpha = 93.5^\circ$	-342.33382	-342.39728	
PH_3	$D_{3h}, r = 2.58$	-342.27960	-342.33220	
PH_3	$D_{3h}, r = 2.685$		-342.32722	-342.48710
PH_3	T -shaped (π), ^b $r_{\text{ax}} = r_{\text{eq}} = 2.58$		-342.26301	
PH_3	T -shaped (π), ^b $r_{\text{ax}} = r_{\text{eq}} = 2.685$	-342.21604	-342.26135	-342.42917
PH_3	T -shaped (σ), ^b $r_{\text{ax}} = r_{\text{eq}} = 2.685$	-342.00236	-342.10507	
H_2	$r = 1.40$	-1.12477	-1.12854	-1.16324
PH_5	T -shaped ^c saddle	-343.272	-343.37698	-343.58880
PH_5	concerted saddle (C_{2v}) ^c	-343.275	-343.38339	-343.59850
PH_5	zwitterionic saddle ^c	-343.278	-343.38092	-343.58543
PH_5	supersaddle ^c		-343.37906	-343.59325
PH_5^-	$O_h, r = 2.80$		-343.99222	
PH_5^-	$O_h, r = 2.75$		-343.99039	

^a All distances in a_0 ($1a_0 = 0.529 \text{ \AA}$). ^b (π) and (σ) refer to the configuration with a π or a σ lone pair respectively. ^c As to the geometries see the text.

timized as a function of the other internal coordinates. It then turned out that starting from PH_5 in an orientation appropriate for ee abstraction, on reducing r and enlarging R one cannot help passing through the point that corresponds to PH_5 in an orientation ready for ae abstraction and one must then further follow the ae abstraction path, which we have just learned is WH forbidden.

Of course, as in other cases of processes that are WH forbidden if some symmetry is preserved but which become allowed by symmetry lowering, such as the addition of CH_2 to H_2 or ethylene,¹⁶⁻²⁰ one can find an allowed "distorted" variant of the forbidden least-motion path, i.e., a non-least-motion ae abstraction. Howell⁷ was successful in finding such a path.

Howell's conclusion⁷ that the reaction must proceed as an ae abstraction is at first glance surprising, at second glance convincing, and after more careful thought quite puzzling.

Why should a reaction for which a concerted WH-allowed path exists prefer to go via the distorted version of a WH-forbidden process? Does one really find the path over the lowest saddle point by minimizing the energy as a function of the coordinates that one does not consider explicitly? There are in fact examples where this is not the case,^{16,21} namely when coordinates not considered explicitly are relevant for the reaction. In the present case the question is: can one describe the reaction appropriately by a two-dimensional cut of the surface or must other coordinates be studied explicitly, especially coordinates with respect to which several energy minima exist? This is actually the case here, although various minima with respect to the "other coordinates" for quite different changes in the geometry may be separated by only a very small barrier, like the ~ 2 kcal/mol of the Berry process. Finally, should the reaction follow the lowest energy path if on this path large changes in the "nonrelevant" part of the geometry occur, or should one rather search for a path of minimum geometry changes?

We shall see that Howell's result is conceptually an artifact of the reduction of the process to a two-dimensional hypersurface, while a three-dimensional one would be required, and numerically an artifact of using a basis without polarization functions that is unable to describe the bonding situation in PH_5 appropriately.

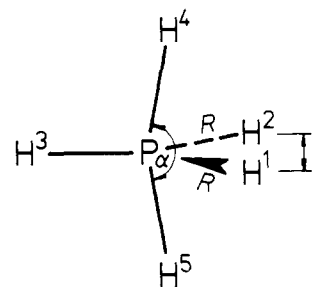
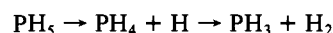
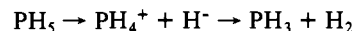


Figure 3. Coordinates varied in C_{2v} geometry. The equilibrium structure of PH_5 corresponds to $\alpha = 180^\circ$, $R = r(\text{PH}^1) = r(\text{PH}^2) = r(\text{PH}^3) = 2.66a_0$, $r(\text{PH}^4) = r(\text{PH}^5) = 2.77a_0$, $r = 4.61a_0$; the saddle point of the concerted reaction is characterized by $R = 2.91a_0$, $r = 1.93a_0$, $\alpha = 172^\circ$; the equilibrium distance in H_2 is $r = 1.40a_0$.

Let us point out that the H_2 abstraction need not be concerted, it might also follow a two-step process, either a homolytic one like



or a heterolytic one such as



One sees easily that the homolytic process cannot compete because PH_4 is not bound with respect to $\text{PH}_3 + \text{H}$.²² We have, using the geometry optimized in ref 22, calculated PH_4 and confirmed the conclusion²² that PH_4 is not bound with respect to $\text{PH}_3 + \text{H}$ (see also Table I).

The heterolytic process turns out (see section VI) to be identical with the non-least-motion variant of the WH-forbidden (ea) abstraction.

Finally, a bimolecular, a catalytic, or an autocatalytic process may have a lower energy than the unimolecular system and may be responsible for the decomposition of PH_5 into $\text{PH}_3 + \text{H}_2$ (or may already prevent its formation) under real chemical conditions.

V. Potential Hypersurface in C_{2v} Geometry

The (ee) abstraction is WH allowed if the PH_3 fragment is left in T -shape with the lone pair in a π orbital (antisymmetric to the plane with respect to which the MO of the removed H_2 is symmetric). In this process C_{2v} symmetry is conserved (see Figure 3) and under this symmetry constraint a smooth transition from

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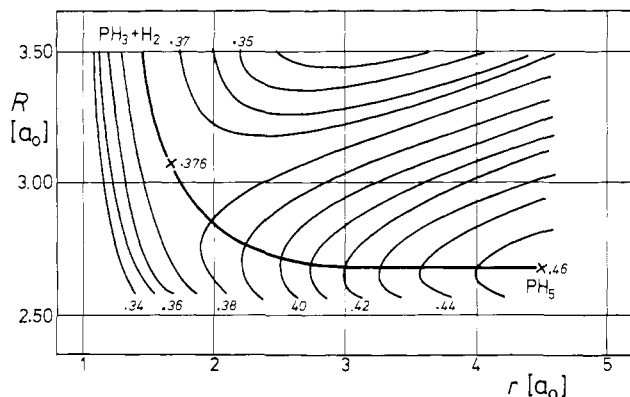


Figure 4. Two-dimensional cut of the potential hypersurface with C_{2v} constraint and the remaining PH_3 fragment in T-shaped form. SCF level with polarization functions. A label such as 0.35 for a contour line means -343.35 hartrees (atomic units). The distance between two consecutive contour lines is 0.01 hartree ≈ 6.27 kcal/mol.

the starting to the final configuration is possible.

We have confirmed that the T-shaped PH_3 has in fact a ground state with a π -type lone pair. The state with a σ -type lone pair (and empty π MO) lies ~ 100 kcal/mol higher. The computed energies of PH_5 , PH_4 , PH_4^+ , and PH_3 in various configurations are collected in Table I.

While with no symmetry constraint at all the number of degrees of freedom for PH_5 is 12, this number is reduced to 8 if C_s symmetry is imposed and to 5 in C_{2v} symmetry. One finds that the PH distances in the remaining PH_3 fragment are not very relevant and that one introduces errors smaller than ~ 1 kcal/mol (see Table I) if one keeps these PH distances constant at $2.685a_0$ and takes the same value in the equilibrium structures of PH_5 and PH_3 . So we are left in C_{2v} symmetry with three relevant geometrical parameters (two of the PH distances kept constant are equal by symmetry), namely (see Figure 3) r , the distance between the two leaving H atoms, R , the distance between P and either leaving H atom, and α , the angle between the two formerly axial bonds.

If we want to leave the PH_3 fragment in T-shaped form we can keep α fixed at 180° and get thus a two-dimensional potential surface. The result from SCF calculations with polarization functions can be seen as a contour line diagram in Figure 4. One realizes that both coordinates are involved in the reactions and that on the least energy path there is from PH_5 to the saddle point a large change of r with little change of R and from the saddle point to the "exit channel" mainly a change of R .

In an oversimplified way one can say that first the H^1PH^2 angle is closed until the distance between H^1 and H^2 is nearly that in isolated H_2 and then the H_2 moves away. The geometry of the saddle point is $R = 3.0a_0$, $r = 1.7a_0$, to be compared with $R = 2.685a_0$ in PH_5 and $r = 1.4a_0$ in H_2 .

Both the barrier height E_{bar} and the exoergicity E_{react} of the reaction (referred to H_2 and PH_3 in its pyramidal equilibrium form as final products) vary considerably with the level of sophistication of the calculation as can be seen from Table II.

We have only redetermined the geometry of the saddle point on level A ($R = 3.0a_0$, $r = 2.3a_0$), since it differs significantly from that obtained on level B (which is a consequence of the large error of E_{react} on level A), but we have not redetermined the saddle point geometry on level C, since we expect it to be very close to that on level B. A few computations in the vicinity of the barrier have confirmed that the correlation energy varies there only slightly.

The sensitivity of both the barrier height and the exoergicity to the level of sophistication is remarkable, though not fully unexpected.

Both PH_5 and the saddle point are hypervalent and can only be described correctly^{1,2} if polarization functions (mainly d AOs on P) are included, while for the normal valent PH_3 polarization functions are rather unimportant.¹ So in a calculation without polarization functions the side $\text{PH}_3 + \text{H}_2$ is much favored and

Table II^a

level	E_{bar}	$E_{\text{react.}} \rightarrow \text{PH}_3(C_{3v})$	$E_{\text{react.}} \rightarrow \text{PH}_3(T)$
A	34	-82	-8
B	50	-43	+42
C	43	-39	+40

^a Energies in kcal/mol. A, B, and C refer to the level of computation as explained at the end of section II. E_{bar} is the height of the barrier for the C_{2v} reaction path with the restriction $\alpha = 180^\circ$, with PH_5 as the reference state. $E_{\text{react.}} \rightarrow \text{PH}_3(C_{3v})$ is the energy of the reaction $\text{PH}_5 \rightarrow \text{PH}_3 + \text{H}_2$ with PH_3 released in its equilibrium structure (with C_{3v} symmetry). $E_{\text{react.}} \rightarrow \text{PH}_3(T)$ is the analogous reaction energy with PH_3 left in T-shaped form.

the exoergicity is overestimated by ~ 40 kcal/mol, while the error in the barrier height is only of the order ~ 10 kcal/mol since at the saddle point geometry polarization functions are important as well and their neglect leads to an error compensation. Inclusion of electron correlation has little effect on the exoergicity, because the number of pairs is conserved, but lowers the barrier since in the saddle point a many-center bond is realized.

One is surprised to find a rather high barrier (43 kcal/mol in CEPA) for a WH-allowed process. But there is an obvious reason for this. PH_3 is namely left in its T-shaped form and its energy is ~ 80 kcal/mol above the pyramidal ground configuration of PH_3 .

The reaction $\text{PH}_5 \rightarrow \text{PH}_3(\text{T-shaped}) + \text{H}_2$ is therefore endoergic by ~ 40 kcal/mol and compared to the final state on the C_{2v} surface the barrier is in fact quite small.

Once PH_3 and H_2 have separated, PH_3 can, of course, relax to its pyramidal equilibrium form, such that the reaction is finally exoergic. Now the question arises whether one can lower the barrier by relaxing the geometry of the PH_3 fragment before the separation of PH_3 and H_2 has taken place.

Such a relaxation requires a lowering of the symmetry from C_{2v} to at least C_s . However, one can even on keeping C_{2v} symmetry relax PH_3 somewhat, namely to its least-energy planar D_{3h} configuration. This is achieved by varying the angle α , defined in the beginning of this section, as well. The result is that for the part of the potential surface between the starting point PH_5 and the saddle point, the optimum α is very close to 180° and that optimization of α has only a very small effect on the energy.

We have reevaluated the saddle point for this three-dimensional potential surface on level B (SCF with polarization functions) and found

$$R = 2.91a_0, r = 1.93a_0, \alpha = 172^\circ$$

One sees that α is much closer to the value of T-shaped PH_3 (180°) than to that for the planar D_{3h} structure (120°) although for isolated PH_3 the latter is ~ 40 kcal/mol lower in energy. A lowering of the energy of this order of magnitude accompanied by a lowering of α toward 120° is observed only in that region of the potential hypersurface where the PH_3 and H_2 subunits are already well separated.

It is obvious that relaxation of the geometry of the PH_3 fragment lowers the energy of this fragment, but diminishes its ability for an attractive interaction with the H_2 fragment, which is optimum for T-shaped PH_3 .

By relaxing the geometry of the PH_3 fragment before one has passed the barrier one loses more than one gains, such that this relaxation is very ineffective.

While the reaction $\text{PH}_5 \rightarrow \text{PH}_3(T) + \text{H}_2$ was endoergic by ~ 40 kcal/mol with a barrier of ~ 43 kcal/mol the reaction $\text{PH}_5 \rightarrow \text{PH}_3(D_{3h}) + \text{H}_2$ is nearly thermoneutral, but the lowering (ΔE_{bar}) of the barrier is rather slight as can be seen from Table III.

A contour line diagram from a level B calculation of the C_{2v} surface as a function of R and r and α optimized is given in Figure 5. It differs from that with the restriction $\alpha = 180^\circ$ mainly in the region of small r . The saddle point is now closer to the equilibrium structure of PH_5 since the reaction is less endoergic.

We have again calculated the energy of the saddle point on levels A and C, reoptimizing the geometry on level A, but assuming

Table III^a

level	$E_{\text{bar.}}$	$\Delta E_{\text{bar.}}$	$E_{\text{react.}} \rightarrow \text{PH}_3(D_{3h})$
A	33	-1	-48
B	46	-4	+1
C	36	-7	+4

^a Energies in kcal/mol. A, B, and C as in Table II. $E_{\text{bar.}}$ is now the barrier height for the C_{2v} reaction path with optimized variable α . $\Delta E_{\text{bar.}}$ is the lowering of the barrier relative to that of Table II (i.e., for $\alpha = 180^\circ$). $E_{\text{react.}} \rightarrow \text{PH}_3(D_{3h})$ is the energy of the reaction $\text{PH}_5 \rightarrow \text{PH}_3 + \text{H}_2$ with PH_3 left in the lowest-energy planar structure (with D_{3h} symmetry).

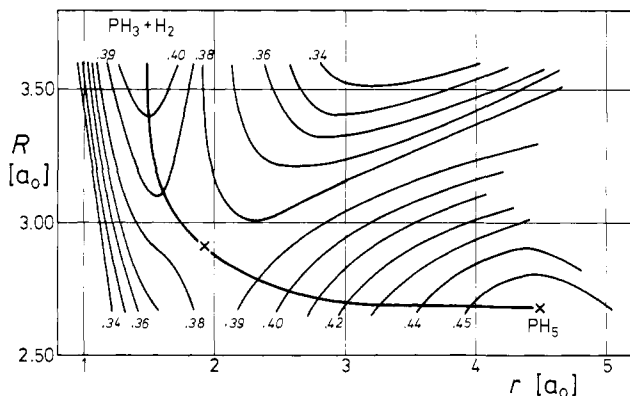


Figure 5. Two-dimensional potential hypersurface in C_{2v} geometry, with α optimized for each pair (R, r) . Computational level and labels of the contour lines as in Figure 4.

on level C the same geometry as on level B. Some calculations on level C in the neighborhood of the saddle point confirmed that on level C its geometry should be very close to that on level B.

VI. Potential Hypersurface in C_s Geometry

To compute a potential hypersurface as a function of all internal degrees of freedom (12) is prohibitive even for such a simple system as PH_5 . From a qualitative discussion of bonding and antibonding interactions one can conclude that the saddle point should have at least C_s symmetry with three H atoms in the symmetry plane and that it will be sufficient to study this C_s surface. One can reduce the number of degrees of freedom from 8 to 6 if one keeps the PH lengths in the remaining PH_3 fragment constant. The choice of these coordinates is illustrated in Figure 6 (note that in a preliminary report of this work²³ β was defined differently).

The two distances R and r are defined as (see Figure 6)

$$R = \sqrt{(r_1^2 + r_2^2)/2}; \quad r = r(\text{H}^1\text{H}^2) \quad (1)$$

$$\text{with } r_1 = r(\text{PH}^1), \quad r_2 = r(\text{PH}^2)$$

R is a measure of the mean PH distance, which has been chosen for convenience sake. One might as well have chosen $(r_1 + r_2)/2$, and take $(r_1 - r_2)/2$ instead of γ .

The energy as a function of R and r , minimized with respect to the four other internal coordinates, is given in Figure 7. It is based on several hundred points on which detailed information is available on request.²⁴

In Figure 7 two regions are marked as shaded to indicate that there the minimum of the energy is realized for a C_{2v} structure. This is the case in the vicinity of the PH_5 equilibrium structure in the ee orientation, but also in the neighborhood of the C_{2v} saddle point studied in the previous section. Therefore the C_{2v} saddle

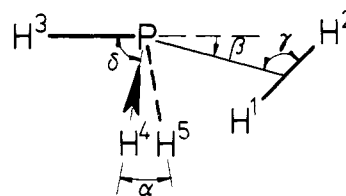


Figure 6. Coordinates used in C_s geometry. With respect to Figure 3 the system is turned by 90° around the PH^3 axis and the two additional parameters β and γ appear. On Figure 3, i.e., in C_{2v} geometry, β is fixed at 0° and γ at 90° . For PH_3 (in its equilibrium configuration) and H_2 at large separation the optimum values are $\alpha = \delta = 93^\circ$, $\beta = 16^\circ$, $\gamma = 81^\circ$. The "zwitterionic saddle" on computational level B has the approximate geometry $R = 3.28a_0$, $r = 2.75a_0$, $\alpha = 120^\circ$, $\beta = -24^\circ$, $\gamma = 60^\circ$, $\delta = 100^\circ$, and the least motion (WH forbidden) approach of H_2 to PH_3 corresponds to $\beta = -57^\circ$.

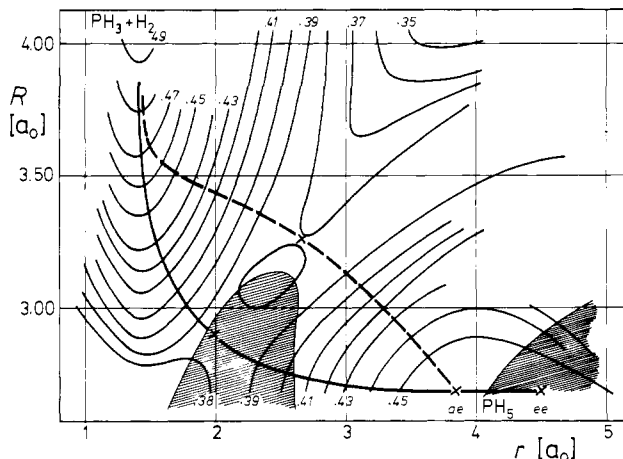


Figure 7. The energy in C_s geometry as a function of the two "reaction coordinates" minimized with respect to the other internal coordinates on the SCF level with polarization functions. Energies as in Figure 2. The thick full line represents the lowest energy path for the concerted reaction, the broken line that via an ion pair. As to the definition of r and R see Figure 6 and eq 1. In the shaded area the lowest energy is realized for a C_{2v} structure.

point remains a saddle point even if one allows for symmetry lowering. However, since it is close to the border of the C_{2v} region—and since this region will probably change with the sophistication of the computation—this result should not be taken too literally. We cannot exclude a slight distortion of the saddle point to C_s , but there is hardly the possibility of lowering its energy significantly.

It is surprising that on the path from PH_5 to the saddle point there is a region where the C_{2v} structure does not have the lowest energy. It is even more surprising that there is a second saddle point of almost the same height, but of very different geometry. It is most surprising that the region between and around these saddle points is extremely flat, i.e., that the geometry of the "transition state" is extremely nonrigid.

To understand the reaction better we want now to look at it from the other side, i.e., from separated $\text{PH}_3 + \text{H}_2$ approaching each other. The least motion (WH forbidden) path would correspond to $\beta = -57.25^\circ$ and $\gamma = 90^\circ$ (see Figure 6). On this path there is a strong closed-shell repulsion between the lone pair of P and the H_2 molecule. One can reduce this repulsion if one allows for a charge-transfer interaction.

In the reaction $\text{CH}_2 + \text{H}_2$ ^{16,17} (or $\text{CH}_2 + \text{C}_2\text{H}_4$ ¹⁸⁻²⁰) that is also WH forbidden on the least motion path such an interaction is possible in a distorted geometry by charge transfer from the occupied σ MO of H_2 to the unoccupied π MO of CH_2 (electrophilic step: CH_2 acts as electrophile).^{16,18,20} The reaction is then completed by a charge transfer from the lone pair of CH_2 into the σ MO of H_2 (nucleophilic step).

An electrophilic first step is not possible for $\text{PH}_3 + \text{H}_2$, since PH_3 has no unoccupied orbital; however, a nucleophilic reaction

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(24) J. Wasilewski and W. Kutzelnigg, technical report, Ruhr-Universität Bochum 1980, available on request.

step is possible by charge transfer from the lone pair of PH_3 to the antibonding MO of H_2 .

This charge transfer reduces the closed-shell repulsion between H_2 and PH_3 considerably provided they are oriented toward each other in an optimum way. It turns out that this optimum is, for r close to its equilibrium value for isolated H_2 (i.e., $1.4a_0$) and for the PH_3 fragment near to its equilibrium geometry for R between $3a_0$ and $5a_0$, given by $\beta = 16.4^\circ$, $\gamma = 81.2^\circ$. The minimum is flatter for larger R and steeper for smaller R but its position is nearly independent of R , as long as one is sufficiently far from the saddle point. The WH-forbidden least-motion approach would correspond to $\beta = -57.25^\circ$, $\gamma = 90^\circ$ so that the optimum approach of H_2 to PH_3 is rather "from the side", H_2 prefers to be nearly parallel rather than perpendicular to the lone pair of PH_3 .

The just discussed charge-transfer interaction can lead to an addition of H_2 to PH_3 only if in a subsequent step a charge transfer in the opposite direction involving other MOs is possible, namely from the bonding MO of H_2 to an appropriate unoccupied MO of PH_3 . Such an orbital is not available in pyramidal PH_3 .

However, by changing the geometry of the PH_3 fragment one can make it ready for accepting electrons from H_2 . This is possible in the following manner.

As one opens the angle α (Figure 6) from its initial value of $\sim 93^\circ$ to the final value of 180° , the PH_3 fragment becomes T -shaped and the two H atoms of the approaching H_2 become equatorial: on opening the angle α the lone pair of PH_3 becomes more and more π -like and its ability to interact with the σ^* MO of H_2 increases. This interaction is further enhanced if β changes from 16.4° to 0° and γ from 81.2° to 90° . At the same time an unoccupied σ MO at PH_3 pointing toward H_2 appears and can accept charge from the bonding σ MO of H_2 . The electrophilic and the nucleophilic reaction steps are thus possible simultaneously (in the same geometrical arrangement) which is characteristic for a concerted process, as we have seen it from the other side in the preceding section.

There are three coordinates directly involved in this reaction, namely (see Figure 6) R , r and α , while the other coordinates β , γ , and δ vary only slightly, namely β from 16.4° to 0° , γ from 81.2° to 90° , and δ from 93° to 90° , going through a maximum of $\sim 94^\circ$.

The saddle point found for this concerted reaction corresponds to a geometry of PH_5 that has C_{2v} symmetry or is only very slightly distorted from C_{2v} . Only when the PH_3 fragment has nearly the T -shaped structure is the attractive interaction between PH_3 and H_2 so strong that the energy can decrease on further approach of the two subunits.

There is a second possibility for adding H_2 to PH_3 . Again we start with the optimum approach of H_2 to PH_3 that involves a charge transfer from the lone pair of PH_3 to the σ^* MO of H_2 . Rather than wanting H^4 and H^5 to become axial (as in the concerted process) one may want them to become equatorial together with H^2 , such that H^3 and H^1 become axial. For an approach with $\beta = -57.25^\circ$, $\gamma = 90^\circ$ this would just be the WH-forbidden *ae* abstraction, looked at from the opposite side. However, we start with $\beta = 16.4^\circ$, $\gamma = 81.2^\circ$; since we have so far avoided the least-motion path, continuing on this path can only lead to a distorted variant of the (*ae*) process.

Now α has to change only slightly, from 93° to 120° , while β has to change a great deal, namely from 16.4° to -57.25° , which is the optimum for PH_3 in the "ae orientation", such that now β rather than α is the third important coordinate (after r and R) for the reaction.

At the point where we consider the opening of α , the nucleophilic reaction step (charge transfer from the lone pair of PH_3 to σ^* of H_2) has already started. It is enhanced by the opening of α , but (unless we open α to 180° rather than 120°) an electrophilic step cannot follow, since the PH_3 fragment has no unoccupied MO available.

While in the concerted process the two new PH bonds are formed nearly simultaneously, this is now not possible (WH forbidden).

A value of $\gamma < 90^\circ$ implies that one H atom of H_2 (H^2 in Figure 6) is closer to P than the other. On the concerted path γ remains $\sim 90^\circ$, but changing β from 16.4° to -57.25° with $\gamma \approx 90^\circ$ is impossible, for the same reason that forbids the least-motion *ae* process. The only chance for an allowed process consists of changing γ (namely in reducing it to $\sim 60^\circ$) together with β in such a way that when the H_2 "turns around", it does so in such a way that the two H atoms of H_2 have quite different distances to P and that the new PH bonds are formed one after the other.

There is no possibility for an electrophilic reaction step, but the nucleophilic one can continue. It implies a weakening of the bond between H^1 and H^2 and the partial formation of a bond between P and the H atom that is closer to P. At the end of this interaction lies the formation of a PH_4^+/H^- ion pair.

After the ion pair has been formed, a second PH bond involving the H^- can be formed, which is accompanied by a further change of β and γ with β approaching its final value and γ increasing again to reach 90° . The nucleophilic and electrophilic steps of the reaction are now well separated. Separating the two steps is the only possibility of making a symmetry-forbidden reaction allowed by distortion. So the distorted WH-forbidden (*ae*) process turns out to be identical with the heterolytic one that passes over an ion pair transition state.

The saddle point is found to have the approximate geometry $R = 3.28a_0$, $r = 2.75a_0$, $\alpha = 120^\circ$, $\beta = -24^\circ$, $\gamma = 60^\circ$, $\delta = 100^\circ$. The position of the saddle point cannot be determined very accurately since the potential surface is extremely flat in the saddle point region.

From a population analysis and from its dipole moment (4.53 D) one concludes easily that at this saddle point the system is an ion pair PH_4^+/H^- .

One might think that the concerted and the zwitterionic processes are mechanistically so distinct that there are, irrespective of which of the two has the lower barrier, two clear-cut "reaction channels". Unfortunately if one really computes the potential hypersurface this conjecture is not confirmed. The two-dimensional potential hypersurface in terms of r and R with the energy minimized with respect to the other coordinates is given in Figure 7 on the computational level B (SCF with polarization functions). One finds two saddle points with nearly the same energy, but very different geometries and very different dipole moments (concerted 0.62 D, zwitterionic 4.53 D), which are only separated by a very flat "supersaddle point".²⁵ In the region of the two saddle points the surface is extremely flat (consider, e.g., the space between the contour lines 0.38 and 0.39 in Figure 7).

In the saddle point region one has for very large geometry changes only small changes in the energy. This is another aspect of the nonrigidity of the PH_5 system. The saddle point is extremely nonrigid. To switch from the concerted to the zwitterionic transition state costs, at this level (B) of computation, almost no energy.

Before we discuss this potential surface in more detail we have to point out—what is of course not unexpected—that the potential surface is very sensitive to the level of sophistication of the calculation. It is obvious that in a study without polarization function the "zwitterionic transition state" is better described than the concerted one. In fact, Howell⁷ in a study without polarization functions has only found the zwitterionic transition state and has therefore concluded that the system prefers the distorted WH-forbidden over the WH-allowed reaction path.

It is also obvious that electron correlation should stabilize the concerted relative to the zwitterionic transition state, which is confirmed by the calculations. We have not recalculated the whole potential surface on the levels A and C, but only computed the energies of the two saddle points and the "supersaddle point" of level B on the two other levels. One sees from Table IV that on level A (SCF without polarization functions) only the zwitterionic

(25) By this we mean a stationary point of the potential hypersurface with two negative and otherwise positive eigenvalues of the matrix of second derivatives with respect to the internal coordinates. A saddle point has one negative eigenvalue and a (local) minimum only positive eigenvalues.

Table IV^a

level	concerted saddle	"super-saddle"	zwitterionic saddle
A	33		31
B	46	49	48
C	36	39	44

^a Energies in kcal/mol above PH_5 (D_{3h}). A, B, and C as in Table II. "Concerted saddle" means the barrier height for the "concerted" reaction path and "zwitterionic saddle" the one for the zwitterionic reaction path, while "supersaddle" refers to a higher order stationary point between the two saddle points. A supersaddle is only present on level B; the value on level C simply refers to the geometry of level B—"supersaddle".

saddle point seems to survive, but on level C (CEPA with polarization functions) only the concerted one survives.

We conclude that on the highest level of computational sophistication (C) the lowest saddle point (and probably the only one) is that corresponding to the WH-allowed *ee* abstraction.

Nevertheless the region near the saddle point remains rather flat and in a trajectory calculation trajectories over the concerted and over the zwitterionic "transition state" should have comparable importance. The reaction is hence quite complicated.

One also realizes that a three-dimensional potential surface, in terms of α as well as r and R , with the energy minimized with respect to the remaining internal coordinates would be preferable. On this three-dimensional surface the two points corresponding to PH_5 (*ae* or *ee*) in Figure 7 would be quite distant, since *ee* corresponds to $\alpha = 180^\circ$, and *ea* to $\alpha = 120^\circ$. If one follows the least-energy path from PH_5 (*ee*) on the two-dimensional surface of Figure 7, one has to go through the point (*ae*), since if one just closes the equatorial H^1PH^2 angle from 120 to 90° (as one has to do on the concerted reaction path) one raises the energy, while if one relaxes as well all other geometrical parameters, to get PH_5 in its equilibrium structure but with H^1 and H^2 now in an axial and an equatorial position, one gets the equilibrium energy of PH_5 again. Essentially this was noted by Howell,⁷ who concluded that the reaction has to go via an (*ae*) abstraction.

We now find that even if from PH_5 (*ee*) one passes the point PH_5 (*ea*) one has still the choice to continue toward the saddle point for either the concerted or the zwitterionic reaction. In the former case one has to open α again (from 120° to 172°) before it closes toward the equilibrium angle of PH_3 ($\sim 93^\circ$). In the latter case α changes smoothly from 120° to 93° but β varies much and γ goes through a minimum. So both ways are comparably complicated.

Moreover, we have found (though we have not studied this very carefully) that in the region between the two shaded ones on Figure 6, which one has to pass on the concerted path, the C_{2v} structure is (for fixed r , R) at least locally stable with respect to distortions "perpendicular" to the reaction path, although the absolute minimum of the energy (for fixed r , R) is realized for a different orientation of PH_5 . In this case, on the way from PH_5 (*ee*) to the concerted transition state one would not leave C_{2v} geometry on the minimum energy path of the three-dimensional surface, one would instead follow a " C_{2v} bridge" over the " C_s valley".

On the two-dimensional surface two different local minima of $E(\alpha)$ would imply that in some region the surface consists of two different sheets, which are separated by a barrier as a function of α . The concerted and the zwitterionic processes would then start on different sheets and these sheets would merge somewhere near (or beyond) the saddle point region.

It is not quite certain, and hard to check, that this is so, since the barriers between the sheets, if there are any, are supposed to be quite small, i.e., of the order of the inversion barrier, which is only ~ 2 kcal/mol. For the dynamics of the reaction, such small barriers behave nearly as if there were no such barrier at all. On the other hand the passage from one C_{2v} region on a C_{2v} bridge over a C_s valley to another C_{2v} region shows no basic difference, depending on whether or not the bridge "has a railing", i.e., goes through a local minimum with respect to distortion to C_s symmetry.

VII. Conclusions

The study of the system $\text{PH}_5 \rightarrow \text{PH}_3 + \text{H}_2$ reported here has required an enormous computational effort, but it has still not led to a quantitative result. Some uncertainties remain, particularly for the following reasons. (1) Not all geometrical parameters have been varied (additional optimization of $r(\text{PH}^3)$ and $r(\text{PH}^4)$ may lead to changes of ~ 2 – 3 kcal/mol in some regions of the surface) and it has not been studied whether symmetry lowering beyond C_s has any effect (though it is unlikely). (2) The basis, although of reasonable size, is far from complete, and the system PH_5 is very sensitive to details of the basis. (3) Electron correlation has only been taken care of for a few selected points. To do this for the whole surface would have been prohibitive from the point of view of computer time. Fortunately correlation effects are only moderately important.

All details of the computed surface are available on request²⁴ and they may possibly serve as a basis of trajectory calculations.

Nevertheless we think that the qualitative conclusions of this study are more important than the explicit figures, although in order to arrive at these qualitative results a high level of computational sophistication was necessary.

It is most puzzling that such an apparently simple system causes these difficulties, especially that in order to find the reaction path almost all internal degrees of freedom have to be varied and that the reaction path is highly asymmetric. After this experience it is then a new surprise that the lowest saddle point has most likely the rather high C_{2v} symmetry, although this is more or less a matter of chance.

There are two mechanistically quite different "reaction channels", either of which can be understood in terms of (different) chemical concepts, one that is concerted and Woodward–Hoffman allowed, the other which consists of two separated steps, which goes via an ion pair and which is a non-least-motion variant of a WH-forbidden process. The lowest saddle point is that for the concerted process, but the zwitterionic one is only slightly higher and the region between the two saddle points is so flat that they can hardly be regarded as distinct.

Nonrigidity, which is a characteristic feature of PH_5 in its equilibrium structure, shows up again and in a more spectacular form for the transition state. The reaction $\text{PH}_5 \rightarrow \text{PH}_3 + \text{H}_2$ must be accompanied by large-amplitude motions of the "nonrelevant" coordinates and so be quite complicated. There is almost no doubt that trajectories of more concerted and of more zwitterionic type will contribute to the reaction cross section with comparable weight.

What can one conclude concerning (a) the existence and reactivity of PH_5 and a possible path for its synthesis and (b) the reaction $\text{PX}_5 \rightarrow \text{PX}_3 + \text{X}_2$ for say $\text{X} = \text{Cl}$ or $\text{X} = \text{C}_6\text{H}_5$? Unfortunately no fully reliable conclusions are possible. The existence of PH_5 as a molecule in space is unquestionable, because PH_5 is stable with respect to unimolecular decomposition.

The unexpected ease of the heterolytic decomposition let one think that the tendency toward the formation of an ion pair is enhanced by the presence of Lewis acids. As an example, using data from ref 26 we consider the reaction $\text{PH}_5 + \text{BH}_3 \rightarrow \text{PH}_4^+ + \text{BH}_4^-$. It is endoergic by ~ 100 kcal/mol for the ions at infinite separation. For a distance smaller than $\sim 6a_0$ between P and B one expects the reaction to be exoergic (for the reaction $\text{PH}_5 \rightarrow \text{PH}_4^+ + \text{H}^-$ at infinite separation the endoergicity is ~ 170 kcal/mol). So it seems plausible that BH_3 can remove an H^- from PH_5 without a significant barrier. In a second step an H_2 can separate from the ion pair $\text{PH}_4^+/\text{BH}_4^-$, probably also without a significant barrier.

The reaction $\text{PH}_5 + \text{H}^+ \rightarrow \text{PH}_4^+ + \text{H}_2$ requires ~ 234 kcal/mol (CEPA value). This means PH_5 is a relatively strong base, comparable to $\text{N}(\text{CH}_3)_3$. If the protonation of PH_5 were reversible, a relatively strong acid would be required to protonate it, but since it is not reversible, even a very small probability for the "dissociative protonation" of PH_5 may eventually lead to a decomposition of all PH_5 molecules present.

So one cannot exclude that in the presence of catalytic amounts of a Lewis acid (or an ordinary acid) PH_5 is easily decomposed

into $\text{PH}_3 + \text{H}_2$, in spite of its relatively large barrier for a unimolecular decomposition.

It may even be that another PH_5 may take the role of the Lewis acid.

In fact we find (see Table I) that the hydride affinity, i.e., the energy gain in the reaction $\text{PH}_5 + \text{H}^- \rightarrow \text{PH}_6^-$, is ~ 34 kcal/mol, which can be compared with the hydride affinities of H_2CO , 27 kcal/mol,²⁷ or BH_3 , 65 kcal/mol.²⁶ So PH_5 is a moderate Lewis acid, which is also illustrated by the relatively small endoergicity of ~ 130 kcal/mol of the reaction $2\text{PH}_5 \rightarrow \text{PH}_4^+ + \text{PH}_6^-$. We conclude that the presence of another PH_5 molecule may lower the barrier for the zwitterionic desintegration considerably, but we hesitate to confirm this by explicit calculations.

As to the preparation of PH_5 one has to meet two basic difficulties. Starting from $\text{PH}_3 + \text{H}_2$ one has to overcome a barrier of ~ 80 kcal/mol, which is quite hopeless. Starting from $\text{PH}_4^+ + \text{H}^-$ one should get more easily $\text{PH}_3 + \text{H}_2$ than PH_5 .

Concerning the reaction $\text{PX}_5 \rightarrow \text{PX}_3 + \text{X}_2$ one notes that this reaction is endoergic for $\text{X} = \text{Cl}$; one should hence rather consider the reverse reaction. Taking the difference in the sign of the

reaction energy into account one should expect a potential hypersurface with a similar qualitative feature, i.e., a flat saddle region with a competition but not a clear distinction of a concerted and a zwitterionic process.

The first reaction step for the addition of Cl_2 to PCl_3 should be easier than that for the addition of H_2 to PH_3 since the antibonding σ^* MO of Cl_2 is much lower in energy such that Cl_2 is more ready to accept charge. This should lower the barrier for both the concerted and the zwitterionic process, but it is hard to predict by simple qualitative arguments which of the two will be lower.

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Registry No. PH_5 , 13769-19-2; PH_3 , 7803-51-2; H_2 , 1333-74-0; PH_6^- , 79839-88-6; PH_4 , 25530-87-4; PH_4^+ , 16749-13-6.

Concerted Dihydrogen Exchange between Ethane and Ethylene. SCF and FORS Calculations of the Barrier

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Abstract: The concerted dihydrogen exchange reaction between eclipsed ethane and ethylene yielding ethylene and ethane is "symmetry allowed". Nonetheless, on the basis of SCF and full optimized reaction space (FORS) MCSCF calculations, a reaction barrier of about 71 kcal/mol is predicted. The electronic rearrangements and the origin of the barrier are analyzed.

The least-motion concerted transfer of two hydrogen atoms from eclipsed ethane to ethylene is symmetry allowed and has been explicitly discussed as a paradigm by Woodward and Hoffman^{2a} and by Goddard.^{2b} Rye and Hansen^{3a} have conjectured such a process to play an intermediary role in the hydrogenation of ethylene over a metal catalyst, supposing that the adsorbed ethylene might have a structure similar to that of ethane. Doering and Rosenthal^{3b} have observed dihydrogen exchange from *cis*-9,10-dihydronaphthalene to various olefins. The analogous hydrogenation of olefins by diimide⁴⁻⁶ has long been recognized for its versatility and stereospecificity.

Nonetheless, the theoretical investigation reported here reveals the existence of a substantial barrier for the concerted exchange

of hydrogens from ethane to ethylene.

In agreement with the reasoning by Woodward and Hoffman^{1a} we assume a concerted movement of both hydrogens, maintaining C_{2v} symmetry throughout. We further assume that the activated complex of highest energy occurs for the transition state with D_{2h} symmetry shown in Figure 1 and verify afterward that this geometry is indeed a saddle point on the energy surface.

In the present case, the "conservation of symmetry" is equivalent to the statement that a single-determinant Hartree-Fock SCF wave function can be used to represent the system at all stages of the reaction in the sense that the occupied MO's of the reactants deform continuously and smoothly into the occupied MO's of the products. Accordingly, we first performed ab initio calculations at the SCF level for the reactant/product geometry and for the transition-state geometry. Subsequently we tested the validity of this approximation and, hence, the applicability of the concept of symmetry allowedness by carrying out full optimized reaction space (FORS) multiconfiguration SCF (MCSCF) calculations which allow for the dominant electron correlation effects on the calculated barrier. They also deepen the understanding of the electronic rearrangements.

Method of Calculation

Glossary. The following terms and abbreviations will be used in the sequel.

PAO, primitive atomic orbital: an exponential or a Gaussian multiplied by powers of x , y , and z or by a solid spherical har-

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