Physical Chemistry

Double proton shifts in associates of formic acid with hydrides of third period elements

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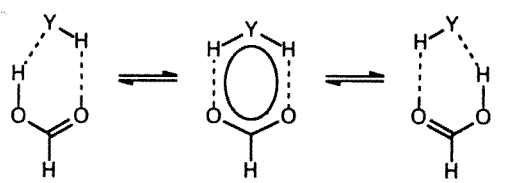
The mechanisms of double proton shift in associates HC(O)OH · · · X of formic acid with hydrides (X = SiH_4, PH_3, PH_5, H_2S, SH_4, ClH, and ClH_3) were studied by the *ab initio* method (SCF/3G*). The activation barriers to this reaction in associates with PH_3, H_2S, SH_4, ClH, and ClH_3 are equal to 68.3, 10.0, 26.0, 1.0, and 0.4 kcal mol^{-1}, respectively. For X = SiH_4 and PH_5, transition states for the double proton shift were not determined, and in all of the other cases studied they are synchronous (concerted or one-step).

Key words: formic acid, associate, potential energy surface, reaction path, activation barrier.

The understanding of reaction mechanisms in enzymatic systems and dynamics of their functioning depends on their modeling by simple molecular systems that adequately reflect the main dynamic parameters of the cooperative processes. Intermolecular proton transfer plays one of the key roles in these processes. Previously,[1,2] we have studied the mechanisms of double proton shift in associates **1A** of formic acid and hydrides of second period elements YH (Y = CH_3, NH_2, OH, and F) and have shown that the activation barrier to reaction (1) correlates with the electronegativity of the central atom of the YH molecule (proton shift mediator), and the ease with which the reaction is carried out is controlled by stereochemical correspondence rules.[3]



1A **1C** **1B** (1)

Y = SiH_3 (**a**); PH_2 (**b**); SH (**c**); Cl (**d**); PH_4 (**e**); SH_3 (**f**); ClH_2 (**g**)

Similar study of regularities of reaction (1) in the case of hydrides YH of third period elements is of interest, because these regularities make it possible to analyze the possible role of a decrease in electronegativity of the central atom of the YH molecule-mediator. In addition, the ability of third period elements to form

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hypervalent structures allows one to check in detail the efficiency of the hypothesis of stereochemical correspondence. In this work, the transport properties of SiH_4, PH_3, PH_5, H_2S, H_4S, ClH, and ClH_3 molecules in reaction (1) were studied by *ab initio* calculations. In this series, the hydrides PH_5, H_4S, and ClH_3 are hypothetical (experimentally unknown); nevertheless, their theoretical structures agree with the experimental data on hypervalent compounds of third period elements and correspond to minima on the corresponding potential energy surfaces (PES).

It was not our purpose to determine the exact quantitative parameters of proton shifts. Therefore, reaction (1) was studied by the *ab initio* method (SCF) in the minimum STO-3G* basis set[4] including d-AO of atoms of third period elements. Although this basis is insufficient for prediction of exact geometric and energy parameters of the associates studied, it demonstrated its satisfactory applicability and reliability for qualitative analysis of the topology of the PES and reaction paths of double proton shifts in neutral systems.[1,2,4–6]

Calculation procedure

All calculations were performed on an IBM PC-486 by the restricted Hartree—Fock method (SCF/3G*),[4] using the Micromol-5 program.[7] For quantitative estimates of the geometric parameters of hypervalent structures in accordance with experimental data, it was necessary to use valence-split basis sets comprising necessarily d-orbitals of third period atoms.[4] Therefore, the STO-6-31G* basis set was used in calculations of the hydrides PH_5, H_4S, SH_5^+, ClH_3, and ClH_4^+.[4]

Complete optimization of geometry of the states corresponding to the saddle points ($\lambda = 1$, hereinafter λ designates the number of negative eigenvalues of the Hesse matrix in the given critical point[5,8]) was performed until the gradient reached a value of 10^{-6} Hartree $Bohr^{-1}$ and those related to energy minima ($\lambda = 0$) on the PES (due to the very slow convergence of the optimization process) reached 10^{-4} Hartree $Bohr^{-1}$. The matrix of force constants was numerically calculated by the three-point scheme with an increment of 0.001 Å by a program incorporated into Micromol. Structures corresponding to energy minima on the PES were determined by the method of steepest descend (movement along the gradient line) from the saddle point (transition state) to the adjacent critical (saddle or minimum) point, when the gradient reaction path[8] connecting the minima with the corresponding saddle points is simultaneously fixed. The initial direction of the gradient line was specified by a slight shift along the direction of the transition vector of the corresponding transition structure.

The superposition error of calculation of the stabilization energy of associates with respect to the individual molecules of formic acid and the carrier was not taken into account, because intra-association reaction paths were mainly studied rather than dissociation limits, for which account of this error is most important.[4] We did not consider also the influence of tunneling effects on the mechanism and energy of the reactions studied, because it can be expected that these effects are negligible due to the substantial contribution, to the reaction coordinate, of motion of all multielectron atoms in the system studied.[9]

Results and Discussion

Transport properties of hydrides SiH_4, PH_3, SH_2, and ClH in double proton shift reactions. The calculations show that all associates **1A** except for **1Aa** correspond to energy minima ($\lambda = 0$), and symmetric structures **1C** except for **1Ca** correspond to saddle points ($\lambda = 1$) on the PES. The calculated energy and geometric parameters of the ground and transition states of **1A** and **1C** are presented in Table 1 and in Figs. 1 and 2.

System **1Aa** does not correspond to a minimum on the PES, but rather to individual molecules of formic

Table 1. Total (E_{tot}) and relative (ΔE) energies calculated by the *ab initio* method (SCF/3G*), the number of negative eigenvalues of Hessian (λ), and lowest (ν_1 and ν_2) or imaginary (iv) frequencies in associates **1A**, transition structures **1C**, and molecules

Structure	$-E_{tot}$ (au)	δE^a /kcal mol^{-1}	λ	iv(ν_1,ν_2) /cm^{-1}
1Aa	474.20697[b]	0	—	—
1Ab	524.93021	0	0	(14; 78)
1Ac	579.61709	0	0	(80; 112)
1Ad	641.44026	0	0	(90; 210)
1Ae	526.01180[b]	0	—	—
1Af	580.59770	0	0	(43; 61)
1Ag	642.30262	0	0	(12; 59)
1Ca	474.06566	88.68	2	i2633.6
1Cb	524.82121	68.40	1	i2341.2
1Cc	579.60122	9.96	1	i386.6
1Cd	641.43869	0.98	1	i127.6
1Ce	525.89075	75.96	2	i2355.4; i53.2
1Cf	580.55622	26.03	1	i557.2
1Cg	642.30195	0.42	1	i7.9
5	473.93311	171.85	2	i4215.1; i557.1
HC(O)OH	186.21788		0	(692; 712)
SiH_4	287.98909	0[c]	0	(1208t)
PH_3	338.70858	2.35[c]	0	(1456; 1504)
PH_5 (D_{3h})	339.79392	0.00[c]	0	(695; 695)
H_2S	393.39377	3.41[c]	0	(1431; 3187)
H_4S (C_{4v})	394.37762	1.38[c]	0	(975; 995)
HCl	455.20665	9.87[c]	0	(3425)
H_3Cl(C_{2v})	456.072208	7.86[c]	0	(1595; 1871)

[a] 1 au = 627.517 kcal mol^{-1}. [b] Total energy of individual molecules of formic acid and hydride. [c] Relative energies of the sum of individual molecules of formic acid and hydride.

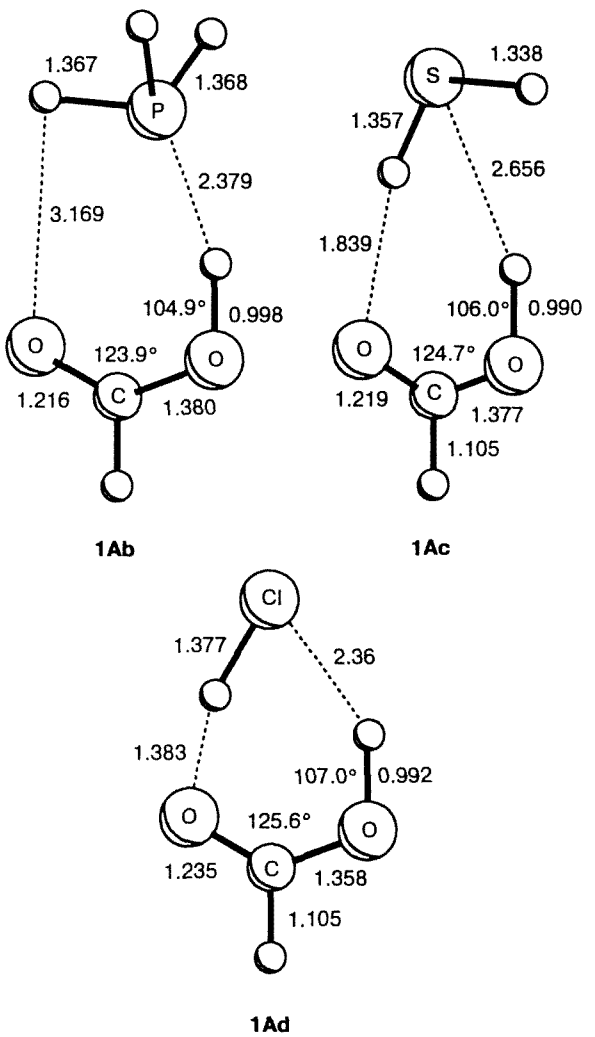


Fig. 1. Associates **1Ab—d** calculated by the *ab initio* method (SCF/3G). Bond lengths are given in Å.

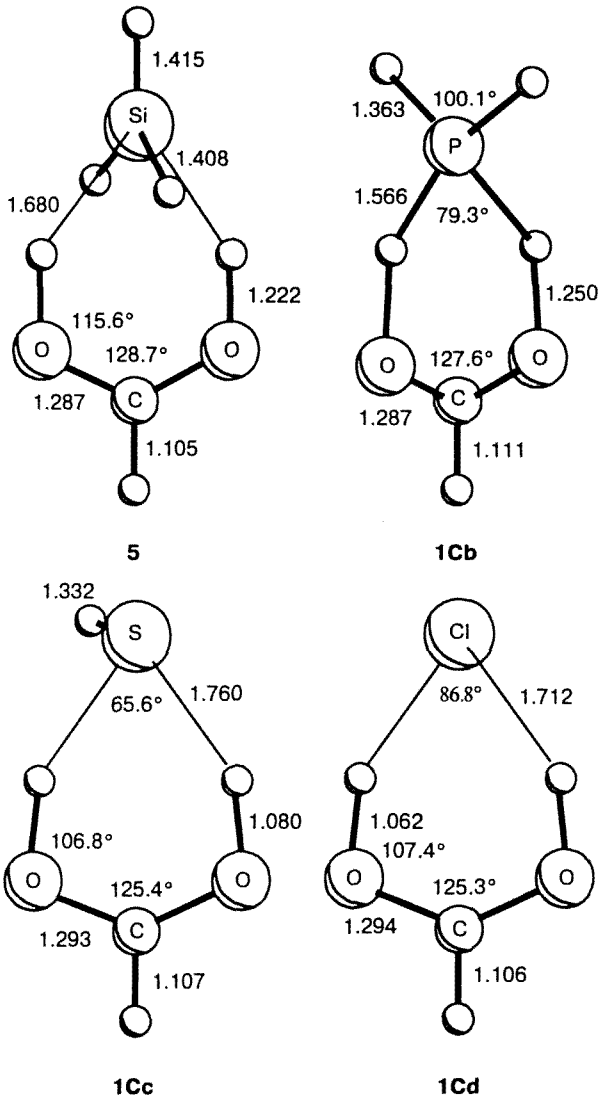


Fig. 2. Transition states **1Cb—d** and form **5** corresponding to the critical point with $\lambda = 2$ on the PES calculated by the *ab initio* method (SCF/3G*). Bond lengths are given in Å.

acid and the hydride SiH_4. Associates **1Ab—d** are the pre-reaction complexes stabilized due to the formation of hydrogen bonds between the molecules of formic acid and YH (see Fig. 1). However, since the superpositional error,[4] which can reach ~1—5 kcal mol^{-1} in minimum basis sets, was not taken into account, the hydrogen bond energies obtained should be treated carefully. This concerns first of all the weak hydrogen bond (~2.3 kcal mol^{-1}) between formic acid and PH_3 in associate **1Ab** that was predicted by calculations.

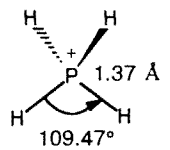
The ease of low-barrier intramolecular rearrangements is determined by the degree of structural resemblance of each reaction unit of the transition state of a given reaction to transition structures of the constituents, "elementary" reactions.[3,10,11] Reaction (1) of 1,3-proton shift passes through the cyclic transition state **1Cb—d** with two bridge hydrogen bonds (see Fig. 2). The YH molecule performs bifunctional (acid-base) catalysis, acting as both a proton donor and acceptor, and cooperatively transfers two protons simultaneously *via* two hydrogen bridges. This reaction can be conventionally divided into three "elementary" reactions: (a) proton transfer from the oxygen atom of formic acid to YH; (b) electrophilic substitution of the hydrogen atom in the YH molecule; and (c) proton transfer from YH to the second oxygen atom of formic acid.

Proton shift from one atom to another presumably occurs *via* the linear transition state.[5,10] However, our calculations showed that considerable deviations from linearity (up to ~30°) in the Cl—H—Cl$^-$ structure result in insignificant changes in the total energy of the system (within 5—10 kcal mol^{-1}). This result agrees well with the experimental[12] and calculated data,[4,10] which indi-

cate that the energies of hydrogen bonds are not very sensitive to angular deformations within the limits mentioned.

Assignment of the second "elementary" reaction to the type of bimolecular electrophilic substitution (S_E2) of the hydrogen atom in the YH molecule is justified by the following considerations.

First, the configurations of YH bonds in transition states **1Cb—d** are close to those determined for structures **2—4** of the corresponding cations PH_4^+, SH_3^+, and ClH_2^+, modeling the simplest transition forms (intermediates) of S_E2 reactions in the case of hydrides of third period elements.



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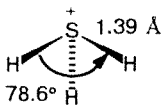

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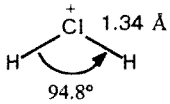

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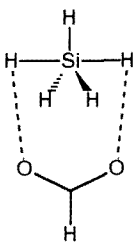
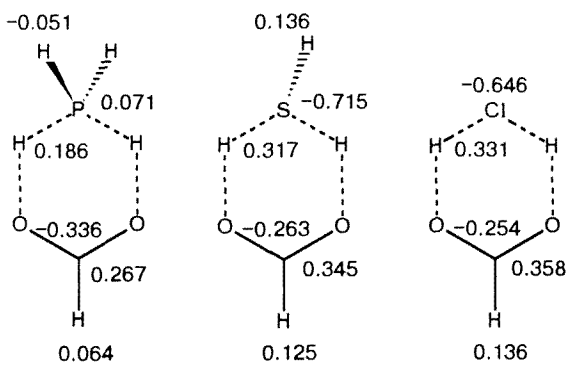


5, C_{2v}

Second, the migrating hydrogen atoms in transition structures **1C** have rather high positive charges.



The decrease in the activation barrier to 1,3-proton shift in the series of **1Ab—d** is due to the increase in the electronegativity of the central atom and, hence, the acidity of the Y—H bond together with an enhancement of the stereochemical similarity to the corresponding structures **2—4** in this series. The proton affinity of the molecules mentioned also increases in this series, although this increase is not monotonic. For example, the affinity values calculated by SCF/3G* (difference in total energies of hydride YH and the corresponding cation YH_2^+) for SiH_4, PH_3, H_2S, and ClH are 175.1, 249.4, 188.7, and 147.1 kcal mol^{-1}. These values are overestimated compared to the experimental ones[13]: ~146.05 (SiH_4); 185.6—196.6 (PH_3); 170.2—196.6 (H_2S); and 119.6—140.3 (ClH) kcal mol^{-1}, but they correctly reflect the trend of their change in this series.

It is of importance that, unlike similar reaction (1), when Y = CH_3,[2] 1,3-proton shift (1) involving silane (Y = SiH_3) cannot be theoretically modelled as either bimolecular electrophilic (S_E2) **1Aa** → **1Ca** → **1Ba** or bimolecular nucleophilic (S_N2) substitution of the hydrogen atom at the central atom of the molecule (proton carrier) *via* the scheme **1Aa** → **5** → **1Ba**, when the stereochemical configuration corresponding to the given reaction type is assigned to the YH group.

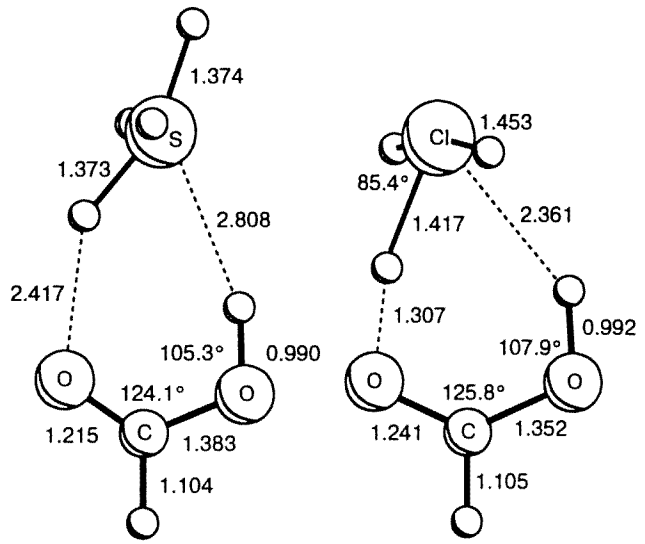
As calculations show, structures **1Ca** and **5** correspond to the critical points with $\lambda = 2$ on the PES and, hence, cannot be transition states in reaction (1). The method of movement along the direction of the eigenvector of the second imaginary frequency from structures **1Ca** and **5** also did not result in localization of the transition state of this reaction.

Transport properties of hypervalent hydrides PH_5, SH_4, and ClH_3 in double proton shift. The case where hypervalent molecules serve as proton carriers is significant for understanding the nature of cooperative proton shift in chemical systems. This is considered by using as an example the expected associates **1Ae—g** in which hypervalent molecules are the simplest hypothetical hydrides of third period elements.

As for lower hydrides, *ab initio* calculations predict that associates **1Af** and **1Ag** correspond to energy minima ($\lambda = 0$), and symmetric cyclic structures **1Cf** and **1Cg** correspond to saddle points ($\lambda = 1$) on the PES, while "adduct" **1Ae** corresponds to the slope point, *i.e.*, it is not characterized by a stationary point on the PES at all. Free movement from this point results in the dissociation of the system to individual molecules of formic acid and the hydride PH_5.

Thus, the calculations showed that associates **1Af** and **1Ag** are stabilized due to the formation of the hydrogen bond between formic acid and hypervalent hydride (Fig. 3), and no stabilizing interaction exists between these reagents in "adduct" **1Ae**. It should be mentioned, as for the simplest hydrides, that the hydrogen bond energies obtained should be treated carefully because the superpositional error was not taken into account in these calculations.[4] This especially concerns the predicted energy of the weak hydrogen bond (~1.4 kcal mol^{-1}) between a molecule of formic acid and SH_4 in associate **1Af**.

The calculated energy and geometric parameters of the ground and transition states **1Af**, **1Ag** and **1Cf**, **1Cg** are presented in Table 2 and Figs. 3 and 4. Structure



1Af **1Ag**

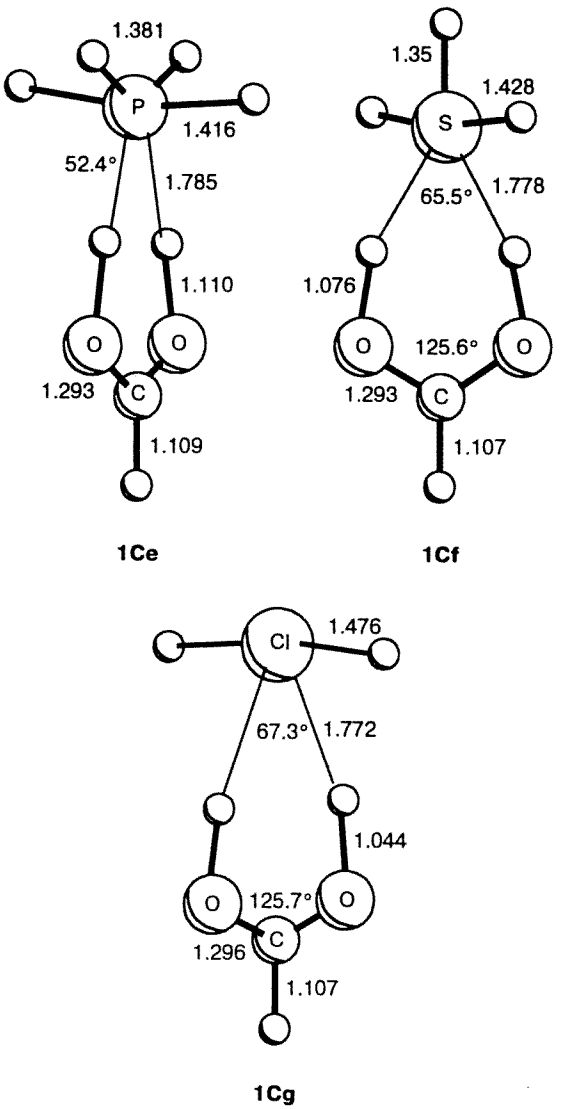
Fig. 3. Associates **1Af** and **1Ag** calculated by the *ab initio* method (SCF/3G*). Bond lengths are given in Å.

1Ae is not presented in Fig. 3 because it does not correspond to the stationary point on the PES.

The calculations predict that cyclic form **1Ce** cannot be the transition state in reaction (1), because it relates to the critical point with $\lambda = 2$. The second negative force constant in structure **1Ce** corresponds to the beginning of proton transfer from PH_5 to formic acid on the path of dissociation of the system to individual molecules PH_3 and $H_2C(OH)_2$. Molecular structures of transitions states of **1Cf** and **1Cg** are of interest. The geometry of these states, as is seen from Fig. 4, are sufficiently well adapted to stereochemistry of three "elementary" reactions described above.

It is noteworthy that transition structure **1Cg** has an extremely low imaginary frequency (i7.9 cm^{-1}), but it corresponds to the saddle point ($\lambda = 1$) on PES. This is confirmed by the calculations of the total energy of the system along the path of the steepest (gradient) descend. These calculations demostrated its monotonic decrease from the point on the PES assigned to structure **1Cg** to the point on the PES corresponding to associate **1Ag**. Transfer of a proton from one atom to the other occurs, as a rule, *via* the transition state close to the linear one.[5,10] According to calculations, the configurations of the O—H—Y and Y—O—H fragments in transition structures **1C** are close to linear with an accuracy of ~30°, and with these deviations from linearity, the changes in the total energy of the system range from 5—10 kcal mol^{-1}.

The hypervalent YH_2^+ fragment is pronounced in transition associates **1C**. In this fragment, the YH bond configuration is close to that determined for hypervalent

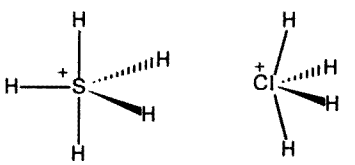


1Ce **1Cf**

1Cg

Fig. 4. Structure **1Ce** corresponding to the critical point with $\lambda = 2$ on the PES and transition states **1Cf** and **1Cg** calculated by the *ab initio* method (SCF/3G*). Bond lengths are given in Å.

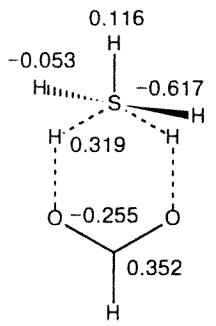
SH_5^+ (**6**) and ClH_4^+ (**7**) cations, which model the simplest transition states (intermediates) of S_E2 reactions for hypervalent hydrides of third period elements.



6, D_{3h} **7**, C_{4v}

The calculated Y—H bond lengths in structures **6** and **7** are ~1.39 and ~1.35 Å, respectively. These compounds have trigonal-bipyramidal structures, and their lone electron pairs play the role of phantom-ligands.

By analogy with protonated forms **2—4**, cations **6** and **7** can be considered as "elementary" transition structures of bimolecular electrophilic (S_E2) substitution of hydrogen atoms at tetra- and tricoordinated sulfur and chlorine atoms, respectively, *via* the scheme of reaction (1). The assignment of the second "elementary" reaction to the type of bimolecular electrophilic substitution (S_E2) of the hydrogen atom in the hypervalent YH molecule agrees with the fact that migrating hydrogen atoms in transition structures **1C** possess rather high positive charges (see charge distribution presented below). It is of interest that the charge distribution over axial and equatorial ligands in the YH_2 fragment corresponds to the polarity rule,[4] controlling charge distribution in structures of the trigonal bipyramid type.



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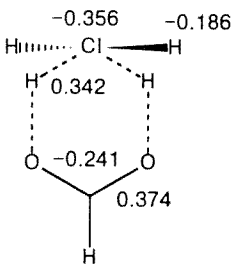

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The decrease in activation barrier to the 1,3-proton shift on going from **1Af** to **1Ag** is caused by the increase in electronegativity of the Y atom and the acidity of the Y—H bond together with the better stereochemical correspondence between structures **1Ag** and **7**. The proton affinity calculated by SCF/3G* is equal to 46.9, 187.8, and 186.8 kcal mol^{-1} for PH_5, H_4S, and ClH_3, respectively.

Thus, the calculations presented show that the principle of stereochemical correspondence for all reaction contacts of "elementary" processes in the given system should be fulfilled for the occurrence of low-barrier synchronized reactions of double proton shift. This principle consists in the approximately linear configuration of hydrogen bridges upon proton shifts and the optimum character of the transition state of the Y atom of the molecule-carrier in the course of the reaction (S_E2). Synchronization (concertedness or concordance) of the shift of two protons in cyclic associates is caused, as in lower hydrides, by the formation of multicentered two-electronic σ-molecular orbitals in transition structures **1C**. The gradient path of reaction (1) for all associates **1A** assumes the usual linear structure and coincides with the path between two minima **1A** and **1B** and transition state **1C**. This path is of minimum energy.[5,8]

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