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A quantum-chemical study of the formation mechanism and nature of *tert*-butyl carbenium ions in 100% sulfuric acid

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Ab initio quantum-chemical calculations reveal that the interaction of isobutene with $H_3SO_4^+$ ions produced by self-dissociation of sulfuric acid occurs virtually without an activation barrier, whereas the reactions involving neutral species of sulfuric acid are characterized by considerable activation barriers: 14.9 kcal/mol at the MP2(full)/6-31+G*//6-31+G* level and 16.9 kcal/mol^{-1} at the MP2(full)/6-31+G*//3-21+G* level. It is also concluded that the species resulting from interaction of isobutane with $H_3SO_4^+$ ions of protonated *tert*-butyl sulfuric acid are ion-molecular complexes which should be considered as *tert*-butyl carbenium ions weakly solvated by H_2SO_4 molecules. Although the concentration of these species in concentrated sulfuric acid is very low, presumably, they play a role of active intermediates in isobutene conversions catalyzed by sulfuric acid.

Keywords: quantum-chemical calculations, sulfuric acid, isobutene, carbenium ions, acid catalysis

1. Introduction

The modern conception of carbenium-ion mechanisms in acid-catalyzed hydrocarbon conversions was formulated by Meerwein, Ingold, Whitmore and others [1–4]. It is mainly based on stereochemistry and distribution of the reaction products. The data on the systems containing sulfuric acid received considerable attention in the above-cited works. Nevertheless, the attempts to detect aliphatic carbenium ions in such systems by spectroscopic methods failed. This implies that carbenium ions are highly active unstable species which are present in reaction media only in very small equilibrium concentrations.

The later discovery of carbenium ions in superacids by Olah et al. [5,6] led to nonobvious extrapolation of the concept that considers alkyl carbocations as the really existing reaction intermediates to other homogeneous and heterogeneous acid catalytic systems. However, for sulfuric acid, such an approach seems to be unjustified, because the strength of sulfuric acid is considerably inferior to that of other superacids. Indeed, the acidity function of 100% sulfuric acid is 12.1 [6], whereas that of HSO_3F containing 14.1 mol% of SbF_5 equals 26.5, i.e., the difference in the proton activities is more than 14 orders of magnitude. This implies that carbocations, which are rather stable in superacid media, may be only short-lived active species in sulfuric acid.

Similar to heterogeneous acid-catalyzed transformations of hydrocarbons on zeolites, experimentally unavailable information about the real nature of these active intermediates could be provided by quantum-chemical calculations. Indeed, as was earlier demonstrated in [7–11], the adsorbed carbenium ions resulting from protonation of olefins, unlike generally accepted schemes, do not exist as real active species but instead are the transition states with properties which are very close to those of free carbenium ions in the gas phase.

The present work presents a similar quantum-chemical analysis for the carbenium ions resulting from olefins in concentrated sulfuric acid. In this connection, below we will discuss isobutene protonation by 98% acid. The choice of this system is dictated by the fact that isobutene is the simplest olefin the protonation of which can yield *tert*-carbenium ions which are more stable than secondary and, especially, primary ions. Earlier such calculations for concentrated sulfuric acid with account of self-protonation and solvation effects were not yet performed.

2. Details of computations

Ab initio quantum-chemical calculations were carried out with the *Gaussian 92* program [12]. The geometries of the investigated structures were fully optimized using the gradient method [13] at the self-consistent field (SCF) theory level with the standard 6-31+G* and 3-21+G* basis sets. For all stationary points found, the calculations of frequencies were performed using a harmonic approach. All transition states found are characterized by one, and only one, imaginary frequency corresponding to the reaction coordinate. The full energies of stable structures and transition states were refined by accounting for the second-order Möller–Plesset perturbation theory [14] (MP2(full)/6-31+G*). Corrections for the zero-point vibration energy were included in the calculated heat effects and activation

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Table 1
Full energies (Å, a.e.) and zero-point energies (ZPVE, a.e.) of the structures under consideration.

	HF/3-21+G*		MP2(full)/6-31+G*//3-21+G*	HF/6-31+G*		MP2(full)/6-31+G*//6-31+G*
	E	ZPVE	E	E	ZPVE	E
i-C_4H_8	−155.24714	0.11599	−156.65386	−156.11459	0.11540	−156.65444
H_2SO_4	−694.57910	0.04142	−698.94158	−698.04876	0.04252	−698.94342
$(H_2SO_4)_2$	−1389.21128	0.08524	−1397.91039	–	–	–
$H_3SO_4^+$	−694.87139	0.05149	−699.20519	−698.32599	0.05349	−699.21019
π-complex i-$C_4H_8{\cdot}H_2SO_4$	−849.84301	0.15960	−855.61224	−854.17214	0.15940	−855.61369
π-complex i-$C_4H_8H_2SO_4{\cdot}H_2SO_4$	−1544.47550	0.20328	−1554.58150	–	–	–
π-complex i-$C_4H_8{\cdot}H_3SO_4^+$	–	–	–	−854.46670	0.16922	−855.90178
TS (H_2SO_4)	−849.80709	0.15559	−855.57703	−854.13117	0.15302	−855.58358
TS ($H_2SO_4{\cdot}H_2SO_4$)	−1544.44408	0.19825	−1554.55098	–	–	–
TS ($H_3SO_4^+$)	–	–	–	−854.46577	0.16526	−855.90502
$C_4H_9HSO_4$	−849.87369	0.16299	−855.64072	−854.19219	0.16266	−855.64227
$C_4H_9HSO_4{\cdot}H_2SO_4$	−1544.50728	0.20680	−1554.61237	–	–	–
$C_4H_9^+{\cdot}H_2SO_4$	−850.19580	0.17243	−855.93503	−854.51501	0.16952	−855.93322

energies. Mulliken charges calculated at the HF/6-31+G* level were used for analyzing electronic structure of the systems under study. Calculated full energies and zero-point vibration energies are summarized in table 1.

3. Results and discussion

As a first step of the problem, we will discuss isobutene interaction with one nondissociated molecule of sulfuric acid. Then, in order to model the effects of self-solvation and self-dissociation occurring in liquid sulfuric acid, we will examine isobutene interaction with a dimeric acid $(H_2SO_4)_2$ and protonated sulfuric acid ($H_3SO_4^+$).

3.1. Isobutene interaction with one molecule of sulfuric acid

According to results of our *ab initio* quantum-chemical calculations (table 2), isobutene interaction with one molecule of sulfuric acid starts with formation of a π-complex (figure 1(a)) which, according to the calculations at the MP(full)/6-31+G*//6-31+G* level, is accompanied by lowering of the system energy by 9.0 kcal/mol. The π-complex further converts to *tert*-butyl sulfuric acid which is a stable covalent compound, since the sum of Mulliken charges at the *tert*-butyl fragment is equal only to $+0.28\ e$, i.e., is much lower than that in a free carbenium ion. The valence angles of the *tert*-carbon atom in *tert*-butyl sulfuric acid ester (101–103°) are also characteristic of a covalent structure (figure 1(c)). The calculated heat effect for the reaction of isobutene addition to one molecule of sulfuric acid is equal to −24.9 kcal/mol at the MP2(full)/6-31+G*//6-31+G* level.

The transformation of the π-complex to *tert*-butyl sulfuric acid proceeds via a transition state (TS) which is depicted in figure 1(b). The geometry of this TS indicates a simultaneous concerted rearrangement of several chemical bonds. In the course of the reaction, the proton of the acid hydroxyl group is transferred to the CH_2 group of isobutene, whereas the olefin *tert*-carbon atom starts to form a bond with the oxygen atom of the S=O group. Simultaneously, the double bond in the hydrocarbon molecule is converted to a single bond, and "switching" of two S–O bonds in the acid molecule occurs. Owing to a high positive charge ($+0.72\ e$), the alkyl fragment in this transition state resembles a free *tert*-butyl carbenium ion. This agrees with its planar structure (the sum of C–C–C valence angles is 357.8°, i.e., close to 360°). Hence, the mechanism of isobutene protonation in concentrated sulfuric acid is similar to that of isobutene protonation on zeolites. Indeed, in the latter case, the most stable structures are also covalent alkoxides, and the structure of the transition state also resembles a free carbenium ion [7–11].

The activation energy of isobutene reaction with one molecule of sulfuric acid calculated at the MP2(full)/6-31+G*//6-31+G* level (14.9 kcal/mol) is high enough and close to the activation energies of isobutene protonation on zeolites. The calculated value is in good agreement with data of [15] according to which the acidities of the high-silica zeolite and of isolated molecule of sulfuric acid in the gas phase are close.

3.2. Isobutene interaction with a dimer of sulfuric acid

It is known that concentrated sulfuric acid is a system with strong intermolecular hydrogen bonds. Such self-solvation may considerably affect the acid reactivity. Therefore, we attempted to elucidate the effect of self-solvation of sulfuric acid on the energy characteristics of its interaction with isobutene taking as a simplest example a sulfuric acid dimer. In order to save computer time, corresponding calculations were performed only at the MP2(full)/6-31+G*//3-21+G* level and compared with the results obtained at the same level for one molecule of sulfuric acid (see table 2).

Similar to the case of one H_2SO_4 molecule, isobutene protonation by sulfuric acid dimer starts with the formation of a π-complex (figure 2). After this, *tert*-butyl sulfuric acid ester associated with the second molecule of sulfuric acid is formed via transition state 2(b). As the results

Table 2
Heat effects of π-complex formation (ΔH^{π}), activation energies ($E^{\#}$), and total heat effects (ΔH) for the reactions of the isobutene with monomeric, dimeric, and protonated sulfuric acid (kcal/mol), corrected for zero-point energies.

	HF/3-21+G*	MP2/6-31+G*//3-21+G*	HF/6-31+G*	MP2/6-31+G*//6-31+G*
Isobutene interaction with H_2SO_4				
ΔH^{π}	−9.2	−9.2	−4.6	−9.0
$E^{\#}$	21.1	19.6	21.7	14.9
ΔH	−26.3	−24.9	−15.1	−24.9
Isobutene interaction with $(H_2SO_4)_2$				
ΔH^{π}	−9.4	−9.5	–	–
$E^{\#}$	16.5	16.0	–	–
ΔH	−27.2	−26.7	–	–
Isobutene interaction with $H_3SO_4^+$				
ΔH^{π}	–[a]	–	−16.2	−23.1
$E^{\#}$	–	–	−1.9[b]	−4.5
ΔH	−45.4	−44.6	−46.3	−42.6

[a] According to the calculation at the HF/3-12+G* level, the reaction occurs without any energy barrier, therefore, a π-complex and transition state do not exist.
[b] $E^{\#}$ without account of ZPVE is equal to 0.6 kcal/mol.

of calculations show, the bond lengths in the π-complex and those in the final product differ only insignificantly (no more than by 0.03 Å) from corresponding parameters of these compounds involved in the reaction with one molecule of sulfuric acid. The difference in the formation energy of the π-complex and the final product is also quite small (only 0.3 and 1.8 kcal/mol, respectively). The final product, *tert*-$C_4H_9HSO_4{\cdot}H_2SO_4$ has a covalent structure. This conclusion is supported by the values of positive charge on the C_4H_9 fragment (+0.3 e) and valence angles of the *tert*-carbon atom (101–114°).

The structure of the transition state (figure 2(b)) is also similar to the corresponding structure found for the reaction with monomeric sulfuric acid. However, the difference in geometry parameters between the two structures is somewhat more pronounced than that in case of the π-complex and the final product. Indeed, the length of the dissociating O–H bond decreases approximately by 0.06 Å, and the length of the forming C–H bond increases approximately by 0.04 Å. The length of the forming C–O bond also considerably decreases.

The calculated activation energy of protonation is only by 3.7 kcal/mol lower than that for the reaction with a single acid molecule. The lowering of the activation energy observed can be accounted for by the stabilization of the more ionic transition state due to solvation by the second acid molecule. We can also assume that the account of a greater number of solvating molecules would result in further decrease in the calculated activation energy. However, because of fast attenuation of Coulombic interaction with the distance, the contribution of each successive H_2SO_4 molecule to the system energy would be smaller than the contribution of the first molecule. Therefore, the solvation of *tert*-butyl sulfuric acid by several sulfuric acid molecules can hardly change significantly the reaction mechanism and result in the formation of *tert*-butyl carbenium ions.

3.3. Isobutene interaction with protonated sulfuric acid

It is known [16] that 100% sulfuric acid is only weakly dissociated and that the equilibrium concentration of $H_3SO_4^+$ ions in the acid is equal to 0.14%. However, this value is high enough to explain the occurrence of chemical reactions involving these species.

Indeed, the results of our calculations show that the mechanism of isobutene interaction with $H_3SO_4^+$ cations differs appreciably from that with the participation of nonprotonated species. A marked difference appears already at the stage of π-complex formation (figure 3(a)). The distance between hydrogen atom of the acid cation and carbon atoms bonded to the cation in this complex is considerably shorter (by 0.4–0.5 Å), and the heat effect of the π-complex formation is markedly higher than these parameters upon interaction with one molecule of nonprotonated acid (−23.1 instead of −9.0 kcal/mol).

The structures of the transition states (figure 3(b)) for the reaction with protonated and neutral acid are also substantially different. Instead of a concerted mechanism, the reaction with protonated acid proceeds mainly via a proton transfer from the $H_3SO_4^+$ ion to the olefin molecule. This results in the activated complex with the distance between the *tert*-carbon atom and the oxygen atom of the sulfuric acid equal to 2.56 Å, while the activation energy of isobutene addition to protonated sulfuric acid sharply decreases. The height of the activation-barrier calculated at the HF/6-31+G* level without accounting for a correction due to the zero-point vibration energy is equal to only 0.6 kcal/mol. Moreover, the account of corrections due to electron correlation in the framework of the MP2 method and of the zero-point vibration energy changes relative positions of the energy levels corresponding to the π-complex and transition state and predicts the absence of an activation barrier.

The heat effect of isobutene addition to a protonated ion of sulfuric acid also markedly exceeds (almost by

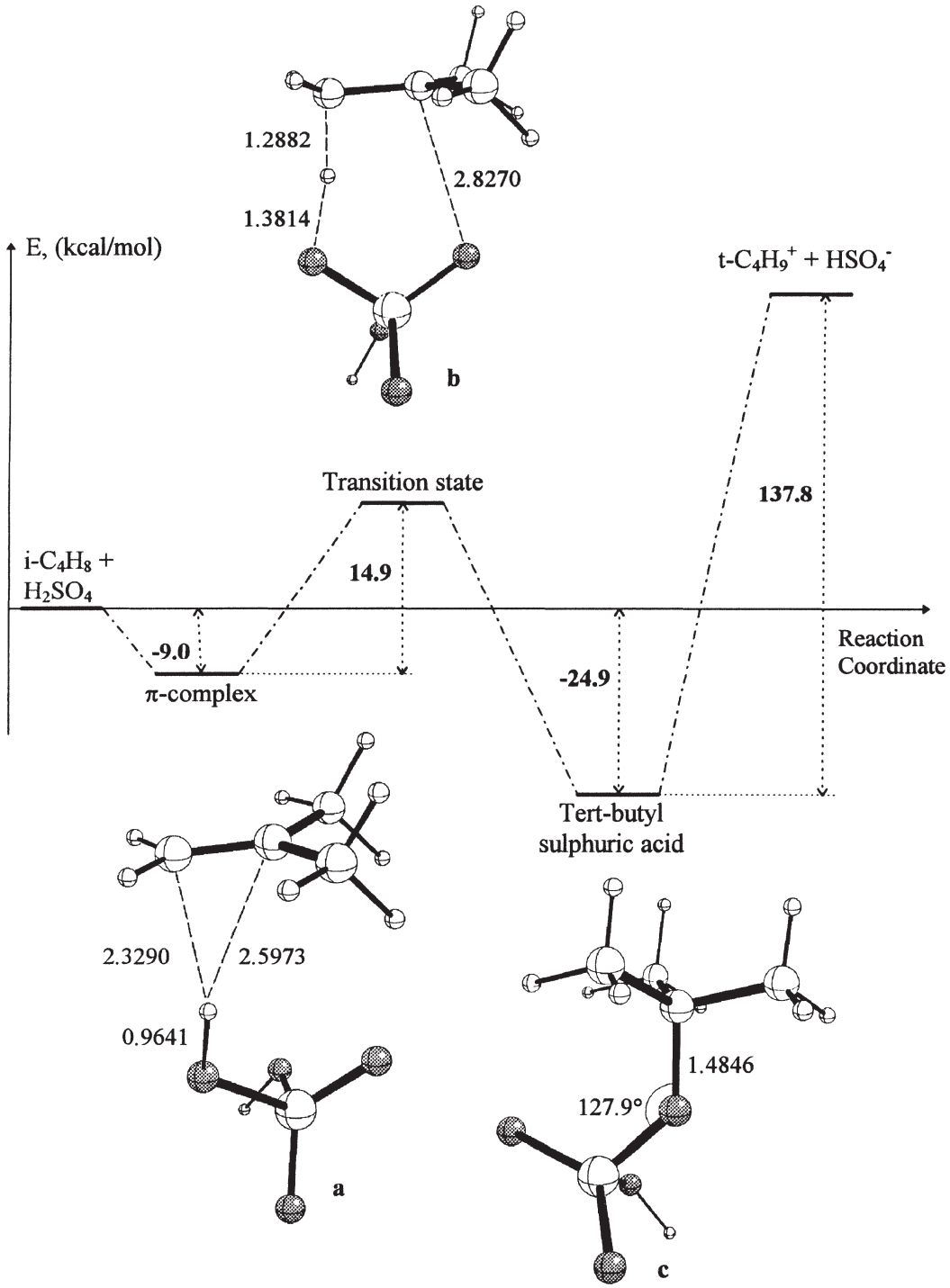

Figure 1. Energy profile of *i*-butene interaction with monomeric sulfuric acid $(H_2SO_4)_2$. (a) π-complex. (b) Transition state. (c) *tert*-butyl sulfuric acid.

20 kcal/mol) the heat effect of reactions with the nonprotonated monomer and dimer of sulfuric acid. The adduct thus formed differs considerably from the covalent ester which is yielded by the isobutene interaction with uncharged sulfuric acid species. It represents an ion-molecular complex (figure 3(c)) which presumably plays an important role in further carbenium-ion conversions of olefins in sulfuric acid. Therefore, we will discuss this complex in more detail in the next section.

3.4. Nature of tert-butyl carbenium ions in 100% sulfuric acid

As we just noted above, the protonated ester produced by isobutene interaction with $H_3SO_4^+$ ions is rather an ion-molecular complex than a covalent structure. Indeed, the length of the C–O bond between the *tert*-carbon atom of the C_4H_9 fragment and the nearest oxygen atom of sulfuric acid in this adduct is 2.5618 Å. This considerably exceeds

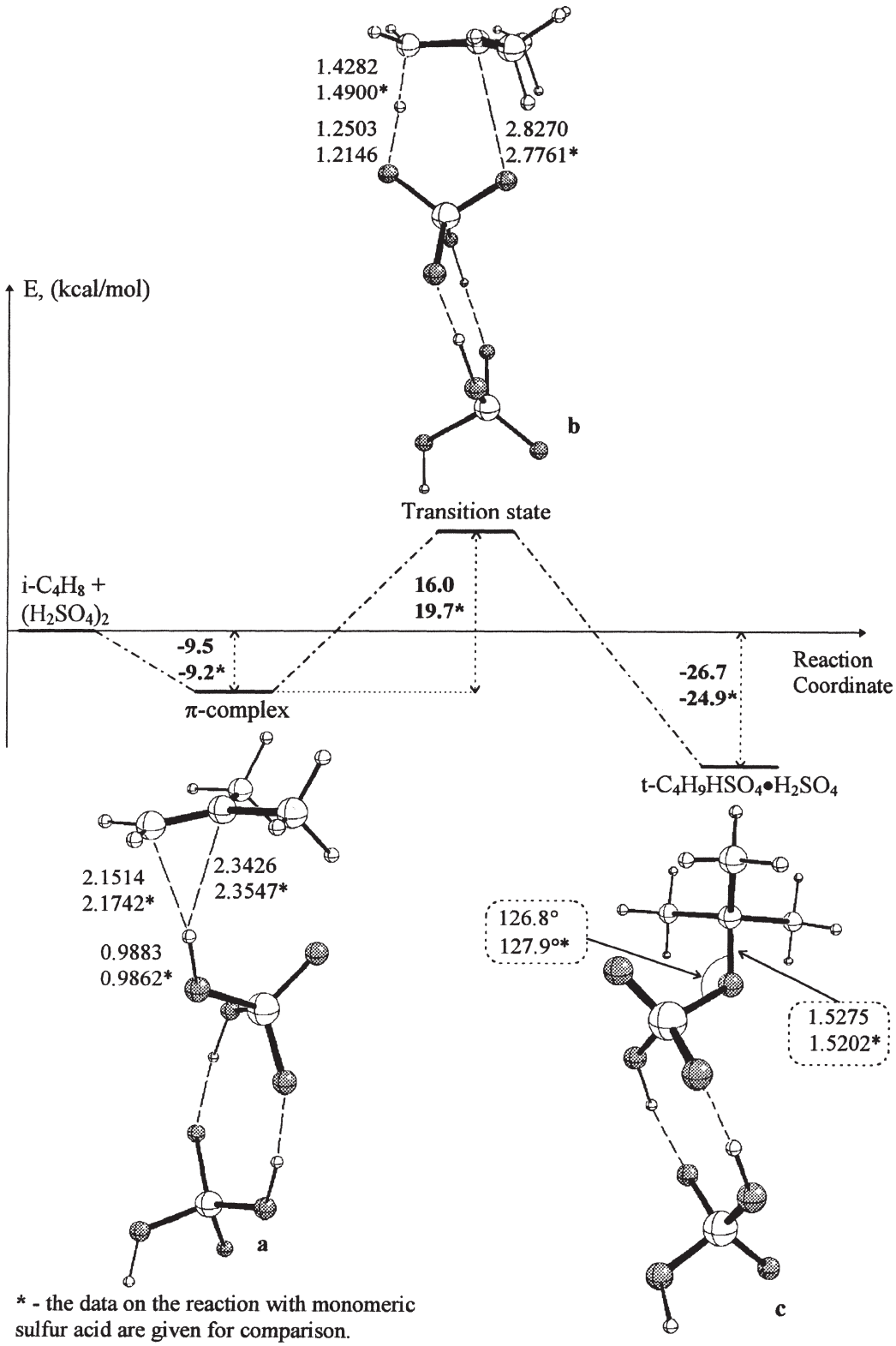

Figure 2. Energy profile of *i*-butene interaction with dimeric sulfuric acid $(H_2SO_4)_2$. (a) π-complex. (b) Transition state. (c) t-$C_4H_9HSO_4 \cdot H_2SO_4$.

the length of the covalent C–O bond resulting in a very broad and shallow minimum of the potential curve. The overall Mulliken charge of the C_4H_9 fragment ($+0.88\ e$) is also very close to the charge of a free carbenium cation. In contrast, the H_2SO_4 fragment has only a small positive charge ($+0.12\ e$), while its geometry only insignificantly differs from that of a free molecule of sulfuric acid.

The results of our calculations also reveal that complete dissociation of the carbon–oxygen coordination bond in such ion-molecular complex to yield *tert*-isobutyl car-

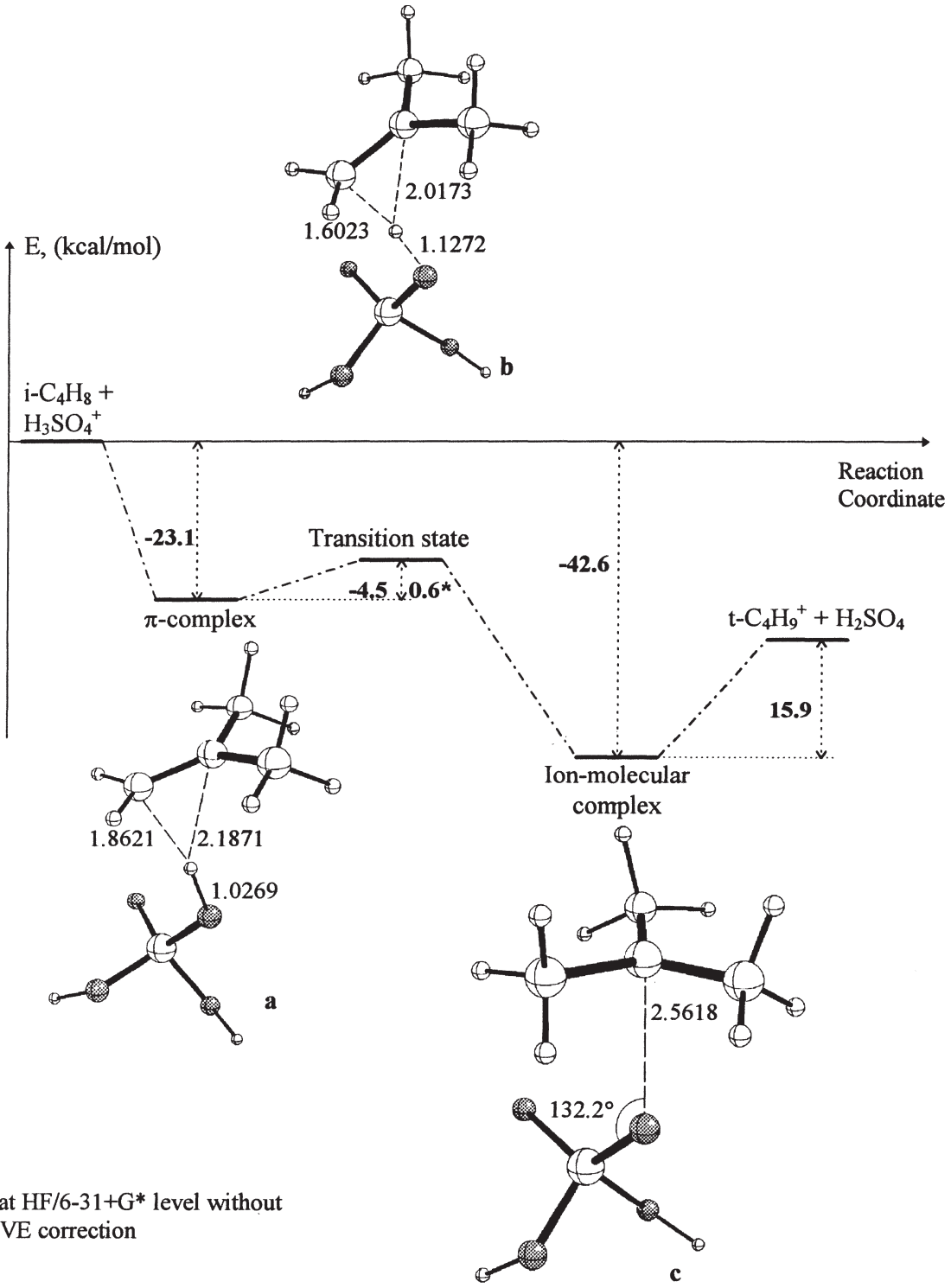

Figure 3. Energy profile of *i*-butene interaction with protonated sulfuric acid ($H_3SO_4^+$). (a) π-complex. (b) Transition state. (c) Ion-molecular complex.

benium ion and a neutral sulfuric acid molecule requires only 15.9 kcal/mol of additional energy. Thus, this ion-molecular complex of figure 3(c) should be considered as a free carbenium ion which is relatively weakly solvated by a molecule of sulfuric acid. Therefore, it is reasonable to assume that these species most likely play the role of active intermediates in carbenium-ion conversions of hydrocarbons catalyzed by concentrated sulfuric acid.

In this connection, the following fundamental difference between the ion-molecular complexes and neutral covalent ester should be underlined. According to our calculations at the MP2(full)/6-31+G*//6-31+G* level, the abstraction of a *tert*-$C_4H_9^+$ ion from neutral *tert*-butyl sulfuric acid requires a tremendous energy of 137.8 kcal/mol. This value is almost ten times greater than the dissociation energy of protonated *tert*-butyl ester. However, it is even more im-

portant that the abstraction of the carbenium ion from neutral *tert*-butyl sulfuric acid is actually not possible, since the stretch of the covalent C–O bond to a length that exceeds its length in the transition state (see figure 1(b)) would rather result in a reverse proton transfer from the *tert*-butyl fragment to HSO_4^- ion than in heterolytic dissociation of the ester. Therefore, instead of heterolytic dissociation, isobutene and a sulfuric acid molecule would be formed. The activation energy of this process is equal to only 30.8 kcal/mol. This value is almost five times smaller than the energy required for abstracting the carbenium ion from the ester. Thus, the neutral ester behaves similarly to isobutene protonation on zeolites, when positively charged carbenium ion-like alkyl fragments are formed only as transition states.

Of course, the above discussion is only a very first approximation, since the additional solvation of carbenium ions with several molecules of sulfuric acid may strongly influence the enthalpy of heterolytic dissociation of protonated ester. Since the corresponding calculations even at the Hartree–Fock level require a tremendous amount of computational time, in this paper we made only a semiquantitative estimation of the additional electrostatic contribution in the subsequent solvation of protonated ester and carbenium ion by sulfuric acid using the continuous COSMO model in the framework of the PM 3 method [17,18]. For this purpose we calculated the electrostatic part of the solvation energy for the reaction:

$$[t\text{-butyl } H_2SO_4]_s^+ \rightarrow [t\text{-butyl}]_s^+ + H_2SO_4 \qquad (1)$$

created by interaction of protonated ester and *tert*-butyl ion with sulfuric acid, which was modeled as a continuous medium with the dielectric constant equal to 110.

The account of this correction transformed the endothermic reaction (1) into the exothermic one with $\Delta H = -14.3$ kcal/mol. Thus, the additional solvation makes the dissociation of protonated esters even more favorable and, therefore, confirms the above conclusion that the protonation of the esters results in *tert*-butyl carbenium ions solvated by the acid.

This conclusion well agrees with the data on two-stage isobutene alkylaton with propylene [19] and with [20] in which the interaction of concentrated sulfuric acid with 1-pentene was studied by ^{13}C NMR. It was shown in the latter work that the interaction of stoichiometric amounts of the acid and olefin yields a mixture of esters with chemical ^{13}C NMR shifts of 75–90 ppm. The esters are stable at room temperature, however, in excess of the acid, they decompose to yield a mixture of paraffin oligomers and cyclopentenes dissolved in sulfuric acid.

The addition of excess acid to the esters is also accompanied by an increase of ^{13}C NMR chemical shifts of carbon atoms in oxo-fragments of the esters from 75–90 up to 82–93 ppm. This effect can be explained by formation of small amounts of protonated esters in excess acid, which are characterized by much greater chemical shifts, and by the averaging of chemical shifts of the esters and protonated esters due to a fast proton exchange between these species.

Indeed, if we assume that the chemical shifts in protonated esters approach the value 300 ppm that are typical of free aliphatic carbenium ions, the concentration of acid solvated carbenium ions can be estimated from the following well known equation for chemical shifts of NMR spectra in conditions of a fast exchange [21]:

$$\delta_{av} = \delta_e N_e + \delta_{pe} N_{pe}, \qquad (2)$$

where δ_{av} is the experimentally observed chemical shift, δ_e and δ_{pe} are chemical shifts in esters and protonated esters, N_e and N_{pe} are mole fractions of the esters and protonated esters in solution.

The concentration of protonated ester in excess of sulfuric acid estimated from this equation does not exceed several percent. This value is approximately by an order of magnitude higher than the concentration of $H_3SO_4^+$ resulting from self-dissociation of sulfuric acid and appears to be quite reasonable taking into account a higher basicity of the esters compared to that of sulfuric acid. Thus, the above results explain well both the experimentally observed ^{13}C chemical shifts and the rather low concentration of acid-solvated carbenium ions in solution, while the carbocations solvated by sulfuric acid are present in excess acid only in very low equilibrium concentrations. These species can be either produced by the direct reaction of olefins with protonated sulfuric acid or by protonation of covalent alkyl sulfur esters with excess of the acid. Most likely, this conclusion is of a more general nature and is equally applicable to formation of alkyl carbenium ions in liquid hydrofluoric acid or in other superacidic systems.

4. Conclusions

(1) The most plausible active species, which is responsible for the reaction of isobutene with sulfuric acid, is the protonated acid. The quantum-chemical calculations indicate that the isobutene interaction with these species yielding protonated *tert*-butyl sulfuric acid occurs virtually without an activation barrier. However, due to the weak self-dissociation of sulfuric acid, the equilibrium concentration of protonated *tert*-butyl sulfuric acid in excess of concentrated acid is very low.

(2) The geometry and electronic structure of protonated *tert*-butyl ester of sulfuric acid represents a weak ion-molecular complex of *tert*-$C_4H_9^+$ with an H_2SO_4 molecule. The properties of the alkyl group in this adduct and in neutral *tert*-butyl sulfuric acid are quite different. In the former, the acid molecule is weakly bonded to the carbenium ion. In the latter, the covalent isobutyl group is strongly bonded to the acid residue and cannot be abstracted by a heterolytic reaction.

(3) The formation of solvated *tert*-butyl carbenium ions and of related derivatives of other hydrocarbons can re-

sult from both the olefin interaction with protonated sulfuric acid and the protonation of covalent alkyl sulfur esters with excess acid. Carbocations solvated by sulfuric acid may play a role of active intermediates in carbenium-ion hydrocarbon conversions catalyzed by sulfuric acid. In accordance with the experimental data, the active ionic intermediates are formed in rather low concentrations which are sufficient for catalysis only in excess of sulfuric acid.

(4) Carbenium ions produced in excess of sulfuric acid and on the zeolite surface are quite different. The former are intermediates solvated by sulfuric acid which actually exist. The latter are the transition states which are formed from covalent alkoxyl groups by thermal excitation.

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