Kinetics and Catalysis, Vol. 42, No. 3, 2001, pp. 411–417. Translated from Kinetika i Kataliz, Vol. 42, No. 3, 2001, pp. 456–463.

Quantum-Chemical Study of Alkyl Carbenium Ions in 100% Sulfuric Acid

V. N. Solkan, I. V. Kuz'min, and V. B. Kazanskii

Zelinskii Institute of Organic Chemistry, Russian Academy of Sciences, Moscow, 119991 Russia

Received March 14, 2000

Abstract—A quantum-chemical study of neutral and protonated monoalkyl sulfates $RHSO_4$ and $[RH_2SO_4]^+$ (where R = CH_3, C_2H_5, *iso*-C_3H_7, and *tert*-C_4H_9) is carried out. Calculations are performed using the Hartree–Fock method in the 6-31G** and 6-31++G** basis sets taking into account electron correlation according to the Müller–Plesset perturbation theory MP2/6-31+G*//6-31+G*. Protonated *tert*-butyl sulfate was also calculated by the DFT B3LYP/6-31++G** method. It was found that monoalkyl sulfates are covalent compounds, and the complete abstraction of alkyl carbenium ions from them has substantial energy cost: 196.4, 161.7, 150.8 and 136.0 kcal/mol, respectively. Protonated methyl and ethyl sulfates are also covalent compounds according to the calculation. They have lower but still high energies of heterolytic dissociation (65.0 and 33.5 kcal/mol, respectively). The energy of R^+ abstraction from protonated isopropyl sulfate is much lower: 23.6 kcal/mol. The main covalent state and the ion–molecular pair, which is a carbenium ion $[C(CH_3)_2H]^+$ solvated by the H_2SO_4 molecule, have about the same energy. The ground state of protonated *tert*-butyl sulfate corresponds to the ion–molecular complex $[C(CH_3)_3^+ H_2SO_4]$ with still lower energy of carbenium ion $[C(CH_3)_3]^+$ abstraction, which is equal to 10.0 kcal/mol. Calculation according to the DFT B3LYP/6-31++G** method shows the absence of a minimum for the protonated *tert*-butyl sulfate with a covalent structure on the potential energy surface.

INTRODUCTION

The catalytic conversion of olefins in the presence of anhydrous sulfuric or hydrofluoric acid is traditionally considered as a classic example of the carbenium-ion reaction. Whitmore, Ingold, and other researchers, who used the data on the stoichiometry and composition of products, developed the currently accepted theory of carbenium-ion mechanisms of acid-catalyzed hydrocarbon conversions [1–4]. Data obtained for the olefin–sulfuric acid system fill an important place in the cited works. Available experimental data suggest that the interaction of olefins with H_2SO_4 or HF first leads to the formation of alkyl sulfates or alkyl fluorides, respectively [5–10]. Nevertheless, the classic scheme of acid-catalyzed olefin conversion is usually described as a set of the following elementary reactions: chain initiation by the formation of carbenium ions via olefin protonation; chain growth with various secondary reactions and rearrangements, which accompany carbenium-ion polymerization; and chain termination by intramolecular hydride transfer from olefin molecules to carbenium ions [11, 12]. The type of acid determines reactivity of aliphatic carbenium ions. Convincing evidence for that was found in the studies of H–D exchange in isobutane for D_2SO_4 [13], DF/SbF_5 or FSO_3D/SbF_5 [14].

A systematic ^{13}C NMR study of olefin transformations in sulfuric acid has begun recently [15, 16]. The ^{13}C NMR spectra revealed that the coupled polymerization of pentene-1 in 95% sulfuric acid is a true carbenium-ion reaction, which occurs via the formation of protonated sulfates. Protonated sulfates are carbenium ions weakly solvated by sulfuric acid. However, attempts to detect aliphatic carbenium ions in these systems by spectroscopy were unsuccessful [17]. This indicates that carbenium ions can exist as very unstable species in very low equilibrium concentrations. On the other hand, aliphatic carbenium ions were observed using high-pressure mass spectrometry [18–21].

Therefore, it was interesting to carry out an *ab initio* quantum-chemical study of the states of carbenium ions $C_1^+–C_4^+$ in the media of anhydrous H_2SO_4 using modern model of solvation. This study can provide information on short-lived species and activated complexes, which are inaccessible to experimental and physicochemical methods. Our paper is devoted to these issues and continues a series of our quantum-chemical studies of acid-catalyzed olefin conversions in the presence of various heterogeneous and homogeneous acid catalysts and their roles in carbenium ion reactions.

Earlier, we have carried out the quantum-chemical calculation of neutral and protonated forms of *tert*-butyl sulfate and their complexes with one H_2SO_4 molecule [22]. Our data suggest that isobutene reacts with sulfuric acid to form covalent *tert*-butyl sulfate. In excess sulfuric acid, protonated *tert*-butyl sulfate should be considered as a *tert*-butyl carbenium ion sol-

0023-1584/01/4203-0411$25.00

vated by one H_2SO_4 molecule. The existence of protonated esters in excess sulfuric acid was confirmed by ^{13}C NMR [15, 16]. It was also fund that the addition of excess sulfuric acid to isopropyl sulfate is accompanied by an increase in chemical shifts at carbon atoms participating in the C–OSO_3H bonds from 78 to 86 ppm. This is explained by the formation of protonated esters in small amounts and by averaging of typically very large chemical shifts with the shift of the main body of nonprotonated ester as a result of fast proton exchange.

It is known that the properties of alkyl sulfates depend considerably on the type of alkyl group. For instance, dimethyl and diethyl sulfates are stable chemical compounds and can be distilled without decomposition at 188 and 210°C. At the same time, isopropyl sulfate and *tert*-butyl sulfate are unstable in distillation [23, 24]. Therefore, it was interesting to supplement our earlier quantum-chemical findings for neutral and protonated *tert*-butyl sulfate [22] with calculations of other low-molecular alkyl sulfates. In this work, we calculated $RHSO_4$ molecules with R = CH_3, C_2H_5, *iso*-C_3H_7, and *tert*-C_4H_9 and their protonated analogs $RH_2SO_4^+$. Electronic and geometric structures of these species is analyzed and the energies of heterolytic abstraction of alkyl cations from neutral and protonated esters. For protonated monoalkyl sulfates, we scanned the potential energy surface along the C–O bond (from 1.3 to 2.7 Å).

CALCULATION METHOD

Geometry optimization of the systems under study was carried out using analytical gradients without taking into account point-group symmetries. Most calculations were carried out within the framework of the Hartree–Fock (HF) method in the 6-31G** and 6-31+G* basis sets. To speed up geometry optimization for molecular species in the Hartree–Fock calculation in the 6-31+G* basis set, we used geometry calculated in the 6-31G** basis set. For optimized geometric parameters of stationary points on the potential energy surface, we calculated the matrix of force constants and analyzed normal vibrations. The values of vibrational frequencies were used in the calculation of zero-point energies (ZPE) without correcting multipliers. Absolute energies were corrected within the framework of the second-order Müller–Plesset theory (MP2(FC)/6-31+G*//6-31+G*). To elucidate the effect of electron correlation on geometry optimization of protonated *tert*-butyl sulfate, we additionally carried out DFT (B3LYP) calculations [25, 26] in the 6-31++G** basis set. The electrostatic component of the free energy of solvation ΔG_{el} was estimated using the polarizable continuum model [27] and the HF method. To analyze the electron structure, we used Mulliken charges calculated by the HF method. Reaction enthalpies estimated from absolute energies, which were calculated at the MP2 level in the 6-31+G* basis set. This allowed us to correct partially the error associated with basis incompleteness. To estimate the ZPE component, we restricted ourselves to calculation at the HF level. Absolute energies, ZPE, and the ΔG_{el} components of the solvation energy are shown in Table 1. Based on these data, we calculated the enthalpies of decomposition of neutral and protonated alkyl sulfates with the formation of carbenium ions shown in Table 2. Quantum-chemical calculations were carried out using the programs GAMESS [28], and Gaussian 98 [29] and SGI Power Challenge and Pentium II (300 MHz) computers.

RESULTS AND DISCUSSION

1. Neutral Alkyl Sulfates

Table 3 shows some important geometric parameters calculated for methyl, ethyl, isopropyl, and *tert*-butyl sulfates, charges at the carbon atoms in the C–O and alkyl groups. The results of quantum-chemical calculation show that the above neutral esters are covalent compounds. Moreover, when switching from methyl sulfate to *tert*-butyl sulfate, there are no changes in geometric or electronic structures. This indicates the absence of a noticeable increase in the polarization of electron density and weakening of the C–O bond. Indeed, in this series, the length of the CO bond increases by only 0.049 Å, and the sum of valence X–C–O angles at the central carbon atom of the alkyl group decreases by only 3.3°. The positive charge at the alkyl fragment increases by 0.021e when switching from methyl sulfate ($q(R^+) = 0.333$) to ethyl sulfate ($q(R^+) = 0.354$). When switching to isopropyl and *tert*-butyl sulfate, it even decreases to 0.328 and 0.275, respectively. Similar trends were seen earlier in quantum-chemical studies of alkoxide groups adsorbed on zeolites [30–33].

On the other hand, unlike geometric and electron characteristics of esters considered above, the energies of the complete abstraction of carbenium ions decrease by ~60 kcal/mol in the series from methyl sulfate to *tert*-butyl sulfate (see Table 2). Nevertheless, the heterolytic abstraction of *tert*-butyl cation from *tert*-butyl sulfate has high energy cost (127.3 or 136.0 kcal/mol if calculated by the HF or MP2 method, respectively). Furthermore, the heterolytic abstraction of carbenium ions from alkyl sulfates is impossible because the C–O bond stretch will result in deprotonation of alkyl groups with the formation of corresponding olefins and a sulfuric acid molecule rather than heterolytic dissociation. Indeed, as is seen from Table 4, the calculated reaction enthalpies of monoalkyl sulfate decomposition into an olefin and sulfuric acid are as low as 12–15 kcal/mol depending on the basis set used in the calculation. These values are almost an order of magnitude lower than the corresponding values of heterolytic dissociation. Consideration of the activation energy does not change this situation. For instance, the activation

Table 1. Absolute energies of molecules and ions (*E*, a.u.), zero-point energies (*ZPE*, kcal/mol), and electrostatic components of the solvation energy (ΔG_{el}, kcal/mol)*

Compound	*E*(HF)	*E*(MP2)	*ZPE*(HF)	ΔG_{el}
1. *tert*-Bu–O–S(=O)$_2$(OH)	−854.2027001	–	–	
	(−854.1921928)	(−855.5938138)	(102.1)	12.4
2. [*tert*-Bu–O–S(=O)(OH)$_2$]$^+$	−854.5347488	–	–	
	(−854.5153273)	(−855.8847856)	(106.0)	57.9
3. *tert*-$C_4H_9^+$	−156.4584626	−157.0097177	–	
	(−156.4432127)	(−156.9440769)	(78.4)	57.3
4. *iso*-Pr–O–S(=O)$_2$(OH)	−815.1657600	–	–	
	(−815.1582802)	(−816.4220090)	(83.6)	12.8
5. [*iso*-Pr–O–S(=O)(OH)$_2$]$^+$	−815.4789188	–	–	
	(−815.4617398)	(−816.7111561)	(90.1)	58.6
6. *iso*-$C_3H_7^+$	−117.3937560	−117.7996698	–	
	(−117.3816382)	(−117.7487592)	(59.5)	61.9
7. Et–O–S(=O)$_2$(OH)	−776.1205509	–	–	
	(−776.1156728)	(−777.2438361)	(64.8)	12.7
8. [Et–O–S(=O)(OH)$_2$]$^+$	−776.4305891	–	–	
	(−776.4160074)	(−777.5313826)	(71.7)	60.4
9. $C_2H_5^+$	−78.32059730	–	–	
	(−78.3115048)	(−78.5532615)	(40.4)	68.1
10. Me–O–S(=O)$_2$(OH)	−737.0794072	–	–	
	(−737.0778705)	(−738.0716469)	(45.8)	12.5
11. [Me–O–S(=O)(OH)$_2$]$^+$	−737.3801440	–	–	
	(−737.3707424)	(−738.3542208)	(52.8)	63.8
12. CH_3^+	−39.2362974	–	–	
	(−39.2308862)	(−39.3257792)	(21.2)	76.6
13. H_2SO_4	−698.0528043		–	
	(−698.0487587)	(−698.9247758)	(26.7)	13.8
14. $[HSO_4]^-$	−697.5334910	–	–	
	(−697.5460715)	(−698.4329431)	(18.5)	68.2

* Calculated by the HF method (RHF/6-31G**, RHF/6-31+G*) taking into account electron correlation at the MP2/6-31+G**//6-31+G** level (calculations in the 6-31+G* basis set are presented in parentheses).

energy of *tert*-butyl sulfate decomposition calculated in [22] is 35 kcal/mol, which is much lower than the activation energy of heterolytic dissociation. Thus, the formation of free alkyl carbenium ions from neutral alkyl sulfates by heterolytic dissociation in the gas phase is highly improbable.

Sulfuric acid is a very polar solvent with a dielectric permittivity of $\varepsilon = 110$, and it can substantially decrease the energy of heterolytic dissociation [34]. Indeed, the electrostatic components of solvation energies in the framework of the PCM model calculated for the alkyl carbenium ions, $[HSO_4]^-$ and alkyl sulfates (see Table 1) show that the solvent effect on the heterolytic dissociation of alkyl sulfates is tremendous. It decreases the process energy depending on the type of alkyl fragment compared to the gas phase by 110–145 kcal/mol (Table 2). Nevertheless, even in the case of *tert*-butyl sulfate, the formation of the $[C(CH_3)_3]^+$ ion solvated by sulfuric acid is still substantially endothermic: ΔH_r^l = 9.1 and 17.8 kcal/mol for HF and MP2 methods. The heterolytic dissociation of isopropyl sulfate with the formation of the isopropyl carbenium ion $[C(CH_3)_2H]^+$ is less favorable ΔH_r^l = 21.8 (HF) and 27.9 (MP2) kcal/mol. In the case of ethyl and methyl sulfates, the process probability is still lower. According to MP2 calculation,

Table 2. Differences in absolute energies (ΔE), zero-point energies (ΔZPE), solvation energies $\Delta(\Delta G_{el})$ of reactants and products (kcal/mol), and enthalpies (ΔH_r, kcal/mol) in the gas phase (g) and in the liquid H_2SO_4 (l) for elementary reactions of carbenium ion formation from neutral and protonated alkyl sulfates*

Reaction	ΔE	ΔZPE	ΔH_r^g	$\Delta(\Delta G_{el})$	$\Delta H_r^l = \Delta H_r^g + \Delta(\Delta G_{el})$
tert-$BuOS(=O)_2(OH)$ ⟶ *tert*-$Bu^+ + HSO_4^-$	+127.3(+136.0)	–5.1	+122.2(+130.9)	–113.1	+9.1(+17.8)
[*tert*-$BuOS(=O)(OH)_2]^+$ ⟶ *tert*-$Bu^+ + H_2SO_4$	+14.7(+10.0)	–0.9	+13.8(+9.1)	–13.2	+0.5(–4.1)
iso-$PrOS(=O)_2(OH)$ ⟶ *iso*-$Pr^+ + HSO_4^-$	+144.7(+150.8)	–5.5	+139.2(+145.3)	–117.4	+21.8(+27.9)
[*iso*-$PrOS(=O)(OH)_2]^+$ ⟶ *iso*-$Pr^+ + H_2SO_4$	+19.7(+23.6)	–3.9	+15.8(+19.7)	–17.1	–1.3(+2.6)
$EtOS(=O)_2(OH)$ ⟶ $Et^+ + HSO_4^-$	+162.0(+161.7)	–2.3	+159.7(+159.4)	–123.6	+36.0(+35.8)
$[EtOS(=O)(OH)_2]^+$ ⟶ $Et^+ + H_2SO_4$	+35.0(+33.5)	–4.6	+30.4(+28.9)	–21.6	+8.8(+7.3)
$MeOS(=O)_2(OH)$ ⟶ $Me^+ + HSO_4^-$	+187.6(+196.4)	–6.1	+181.5(+190.3)	–144.8	+36.7(+45.5)
$[MeOS(=O)(OH)_2]^+$ ⟶ $Me^+ + H_2SO_4$	+57.2(+65.0)	–5.0	+52.2(+60.0)	–26.6	+25.5(+33.4)

* Calculated by HF/6–31+G* and MP2/6–31+G* (in parentheses) methods.

Table 3. Some geometric parameters (bond lengths, *R*) and effective charges (*q*) at the carbon atom and alkyl groups

Compound	*R*(C–O), Å	Valence angles, deg			*q*(C), e	*q*(R), e
		∠(C–O–S)	Σ[∠(X–C–X')]	Σ[∠(O–C–X)]		
CH_3OSO_3H	1.4356	119.7	332.5	324.3	–0.350	0.333
$[CH_3OSO_3H_2]^+$	1.4996	123.7	338.3	317.0	–0.354	0.476
$C_2H_5OSO_3H$	1.4508	121.0	334.5	323.1	–0.060	0.354
$[C_2H_5OSO_3H_2]^+$	1.5496	125.5	341.0	314.1	–0.156	0.506
$(CH_3)_2CHOSO_3H$	1.4638	121.4	335.0	322.5	+0.135	0.328
$[(CH_3)_2CHOSO_3H_2]^+$	1.6113	125.3	343.8	311.1	–0.027	0.528
$(CH_3)_3COSO_3H$	1.4846	127.9	335.3	321.0	+0.036	0.275
$[(CH_3)_3COSO_3H_2]^+$	2.5618	132.2	359.0	279.6	+0.377	0.877

ΔH_r^l = 35.8 and 45.5 kcal/mol, respectively. Thus, the electrostatic PCM model of solvation in the case of negatively charged systems with strong hydrogen bonds is usually very inaccurate even if we use a more exact estimate that we obtained earlier [35] for the solvation energy of the $[HSO_4]^-$ anion by sulfuric acid. However, the heterolytic dissociation of *tert*-butyl sulfate remains noticeably endothermic.

2. Protonated Alkyl Sulfates

According to our quantum-chemical calculation, monoalkyl sulfate protonation results in substantial changes of the geometric and electron characteristics (see Table 3). First, this concerns the length of the C–O bond, which noticeably increases in the series of $RHSO_4$ and $[RH_2SO_4]^+$ molecules and ions (R = CH_3, C_2H_5, *iso*-C_3H_7). The sum of valence angles at the central carbon atom of the alkyl group also noticeably increases (by 6.9°), whereas positive charges at alkyl fragments somewhat increase in this series (by 0.476, 0.506, and 0.528e, respectively).

Most pronounced changes in the parameters of alkyl fragments in the $[RH_2SO_4]^+$ cations are observed when switching from the isopropyl to *tert*-butyl group. The C–O bond becomes 1 Å longer. The sum of OCX angles decreases by 279.6°, and the sum of XCX' angles (where X and X' are alkyl substituents at the central carbon atom) becomes close to 360°; that is, the alkyl fragment becomes planar. Thus, protonated *tert*-butyl sulfate transforms from the covalent to ion–molecular complex consisting of a *tert*-butyl fragment with a high positive charge (+0.88e) and a sulfuric acid molecule.

As expected, the calculated energies of complete abstraction of carbenium ions from protonated alkyl sul-

Table 4. Differences in absolute energies (ΔE) and zero-point energies (ΔZPE) of reactants and products (kcal/mol) and enthalpies (ΔH_r, kcal/mol) in the gas phase (g) for elementary reactions of alkyl sulfate decomposition reactions with the formation of alkenes*

Reaction	ΔE	ΔZPE	ΔH_r^g
tert-$BuOS(=O)_2OH \longrightarrow$ *iso*-$C_4H_8 + H_2SO_4$	+15.7(+15.5)	–3.6	+12.2(+11.9)
iso-$PrOS(=O)_2OH \longrightarrow C_3H_6 + H_2SO_4$	+17.7(+19.6)	–3.2	+14.5(+16.4)
$EtOS(=O)_2OH \longrightarrow C_2H_4 + H_2SO_4$	+14.5(+18.9)	–2.8	+11.7(+16.1)

* Calculated by HF/6-31++G** and MP2/6-31++G** (in parentheses) methods.

fates are much lower (more than by 125–131 kcal/mol, see Table 2) than in the case of neutral esters. When switching from protonated methyl sulfate to protonated *tert*-butyl sulfate, the energy of heterolytic dissociation substantially decreases and becomes only 14.7 (HF) or 10.0 (MP2) kcal/mol. This fact suggests that the properties of *tert*-butyl group in protonated *tert*-butyl sulfate are similar to those for the free *tert*-butyl carbenium ion.

In the case of protonated isopropyl sulfate, the energy of heterolytic dissociation is somewhat higher than for protonated *tert*-butyl sulfate: 19.7 (HF) or 23.6 (MP2) kcal/mol. Thus, the results point to the fact that protonated *tert*-butyl sulfate and possibly isopropyl sulfate are carbenium ions that are weakly solvated by sulfuric acid, and can be considered as active intermediates in the reaction of carbenium ion formation.

Our calculation shows that the protonation of methyl and ethyl sulfates in the gas phase is also favorable for the formation of carbenium ions, but this effect is less pronounced. This follows from a small change in the length of the C–O bond and a small increase in the positive charge on the alkyl fragments upon protonation. The energies of heterolytic abstraction of methyl and ethyl carbenium ions from protonated esters are 57.2 (HF) or 65.1 (MP2) and 35 (HF) or 33.5 (MP2) kcal/mol, respectively; that is, they remain rather high. Therefore, carbenium ions are most likely formed from methyl and ethyl sulfates as transition states in the partial weakening of C–O bonds in alkyl groups before deprotonation. This weakening results in the decomposition of esters with the formation of olefins and sulfuric acid.

Because the PCM model used in our study is the continuum model, it does not allow correct estimation of the solvation effect on the value of the activation barrier, especially in the case of charged systems with strong hydrogen bonds. This is why we restricted ourselves to considering thermodynamic parameters that characterize the occurrence of heterolytic dissociation of protonated alkyl sulfates in sulfuric acid.

Note that protonation perturbs geometric and electron parameters and alkyl sulfate bond energies so strongly that even small concentrations of protonated *tert*-butyl sulfate and possibly isopropyl sulfate can be responsible for the occurrence of the corresponding carbenium-ion reactions. In connection with this, we will consider potential energy surface profiles for C–O bond stretching in protonated alkyl sulfates in the next section.

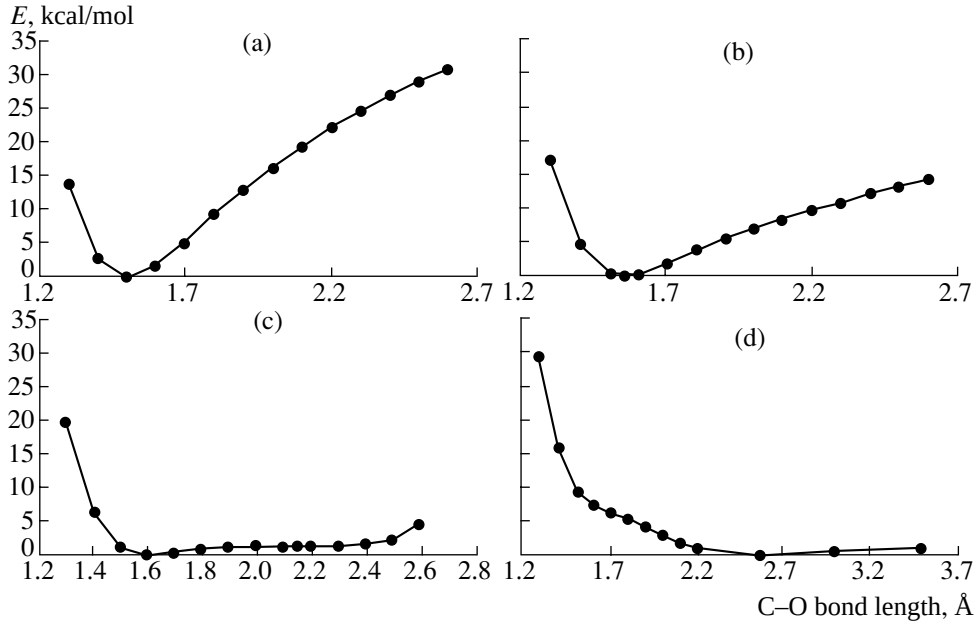
3. Potential Energy Surface Analysis for C–O Bond Stretching in Protonated Alkyl Sulfates

In the previous section, we showed that the process of carbenium ion abstraction from protonated alkyl sulfates strongly depends on the nature of the alkyl radical. Therefore, we scanned the potential energy surface along the coordinate corresponding to the C–O bond stretching from 1.3 to 2.7 Å with a step of 0.1 Å and with a full optimization of other geometric parameters at the HF/6–31+ G* level. The effects of solvation were neglected.

Figure shows that the potential energy surface profile along the coordinate corresponding to the C–O bond stretching strongly depends on the nature of alkyl fragment. The simplest profile is observed for protonated methyl and ethyl sulfates. In both cases, the potential energy curve has pronounced minima corresponding to the covalent C–O distance, which is equal to 1.4996 Å for methyl sulfate and 1.5496 Å for ethyl sulfates. With an increase or decrease in this equilibrium distances, the energy of the system monotonically and rapidly increases. This increase is faster for methyl sulfate than for ethyl sulfate.

Analysis of the potential energy surface profile for the C–O bond stretching in protonated isopropyl and *tert*-butyl sulfates showed that the profile is more complex and differs substantially from that for protonated methyl and ethyl sulfates. The main minimum on the potential energy surface for $[C(CH_3)_2H]^+ \cdot H_2SO_4$ corresponds to the covalent structures with a C–O bond length of 1.6113 Å. With an increase in the distance to 1.9–2.3 Å, the energy of the system does not change and then it starts to increase slowly. An increase in the length of the C–O bond is accompanied by an increase in its polarity. As a result, when the C–O bond length is 2.15 Å, the positive charge of alkyl fragment becomes +0.802e, and the structure of protonated isopropyl sulfate corresponds to the carbenium ion $[C(CH_3)_2H]^+$ weakly solvated by the sulfuric acid molecule.

Finally, the principle difference of the potential energy surface for the C–O bond in protonated *tert*-butyl sulfate is the absence of a minimum correspond-



Changes in the potential energy profile along the coordinate corresponding to the C–O bond stretching in protonated (a) methyl, (b) ethyl, (c) isopropyl, and (d) *tert*-butyl sulfates.

ing to the covalent structure. The energy minimum at a C–O bond length of 2.5 Å corresponds to the ion–molecular complex $[C(CH_3)_3]^+ \cdot H_2SO_4$. The absence of a minimum corresponding to the covalent structure in this system was confirmed by additional density functional theory calculation (B3LYP/6-31++G**).

Thus, analysis of the potential energy surface profile along the coordinate corresponding to the C–O bond stretching in protonated alkyl sulfates reveals substantial differences between esters with different alkyl groups. These differences are not seen when we consider only the ground states. Our findings also suggest that alkyl carbenium ions in chemical reactions with protonated methyl and ethyl sulfates can only be transition states. In contrast, protonated isopropyl sulfate can transform from the ground covalent state to the ion–molecular complex upon excitation. This complex is the carbenium ion $[C(CH_3)_2H]^+$ solvated by a sulfuric acid molecule. For the protonated *tert*-butyl sulfate, the ground state corresponds to the ion–molecular complex $[C(CH_3)_3]^+ \cdot H_2SO_4$, and the covalent structure does not exist at all.

Note that these conclusions agree well with the facts, which are well known from organic chemistry, that chemical properties of (a) methanol and ethanol or ethylene and (b) isopropanol and *tert*-butanol or propylene and isobutylene differ substantially in the presence of sulfuric or other strong acids. In the first case, relatively stable esters are formed. In the second case, the products are formed, which are characteristic of reactions with carbenium ions.

CONCLUSIONS

1. All neutral alkyl sulfates considered in this paper are covalent structures, which are very similar in geometry and electron structure. The abstraction of carbenium ions requires substantial energy and is less favorable than the decomposition into the sulfuric acid molecule and the corresponding olefin.

2. Protonated monomethyl and monoethyl sulfates are also covalent structures, and the abstraction of carbenium ions from them also requires substantial energy. Therefore, in the reactions with their participation, carbocations can only be the fragments of transition states by analogy with the processes of adsorbed carbenium ion formation from the surface alkoxy groups on zeolites. We expect that protonation of esters should result in a substantial decrease of the activation barriers in carbenium ion reactions.

3. The ground state of protonated isopropyl sulfate is a covalent structure. A relatively small stretch of the C–O bond is accompanied by an insignificant change in energy and results in the formation of isopropyl carbenium ions solvated by a sulfuric acid molecule. Therefore, protonated isopropyl sulfate is expected to be active in carbenium-ion reactions.

4. For protonated *tert*-butyl sulfate, the ground state is the ion–molecular complex, which is the *tert*-butyl carbenium ion solvated by a sulfuric acid molecule.

ACKNOWLEDGMENTS

We thank M. Frash and D. Zhurko who took part in quantum-chemical calculation at an early stage of this work. This work was supported by the Russian Founda-

tion for Basic Research (project no. 98-03-32173). Quantum-chemical calculations were carried out in part using the Gaussian 94 [36] program at the Zelinskii Institute of Organic Chemistry, Russian Academy of Sciences (Russian Foundation for Basic Research project no. 98-07-90290).

REFERENCES

1. Whitmore, F.C. and Houk, A.L., *J. Am. Chem. Soc.*, 1932, vol. 54, no. 9, p. 3714.
2. Whitmore, F.C., *Chem. Eng. News*, 1948, vol. 26, p. 668.
3. Whitmore, F.C., *Annu. Rep. Prog. Chem.*, 1933, p. 177.
4. Ingold, C.K., *Structure and Mechanism in Organic Chemistry*, New York: Cornell University, 1969.
5. Schmerling, L., *Ind Eng. Chem.*, 1953, vol. 45, p. 1447.
6. Albright, L.F., Spalding, M.A., Faunce, J., and Eckert, R.E., *Ind. Eng. Chem.*, 1988, vol. 27, p. 381.
7. Albright, L.F., Spalding, M.A., Faunce, J., and Eckert, R.E., *Ind. Eng. Chem.*, 1988, vol. 27, p. 391.
8. Grosse, A.V. and Linn, C.B., *J. Org. Chem.*, 1938, vol. 3, p. 26.
9. Grosse, A.V. and Wackher, R.C., *J. Phys. Chem.*, 1940, vol. 44, p. 275.
10. McElvain, M. and Langsdon, J.W., *J. Am. Chem. Soc.*, 1944, vol. 66, no. 10, p. 1759.
11. Brouver, D.M. and Hogeveen, H., *Prog. Phys. Org. Chem.*, 1972, vol. 9, p. 179.
12. Corma, A. and Martinez, A., *Catal. Rev. – Sci. Eng.*, 1993, vol. 35, p. 483.
13. Stevenson, D.P., Wagner, C.D., Beek, O., and Otvos, J.H., *J. Am. Chem. Soc.*, 1952, vol. 74, no. 13, p. 3269.
14. Olah, G.A., Halpern, Y., Shen, J., and Mo, Y.K., *J. Am. Chem. Soc.*, 1971, vol. 93, no. 5, p. 1251.
15. Kazansky, V.B. and van Santen, R.A., *Catal. Lett.*, 1996, vol. 38, p. 115.
16. Kazansky, V.B., Abennhuis, H.C.L., Vorstenbosch, M.L.V., and van Santen, R.A., *Catal. Lett.*, 2000, vol. 62, p. 100.
17. Kalinovski, H.-O., Berger, S., and Braun, S., *Carbon 13 NMR Spectroscopy*, New York: Wiley, 1988.
18. Field, F.H. and Munson, M.S.B., *J. Am. Chem. Soc.*, 1965, vol. 87, no. 15, p. 3289.
19. Smith, D., Adams, N.G., and Agle, E., *J. Chem. Phys.*, 1982, vol. 77, no. 3, p. 1261.
20. Hiraoka, K. and Kebarle, P., *J. Am. Chem. Soc.*, 1976, vol. 98, no. 20, p. 6119.
21. Dunbar, R.C., Shen, J., and Olah, G.A., *J. Chem. Phys.*, 1972, vol. 56, no. 8, p. 3794.
22. Zhurko, D.A., Frash, M.V., and Kazansky, V.B., *Catal. Lett.*, 1998, vol. 55, p. 7.
23. Nenitescu, C., *Chimie organica*, Bucharest: Inostr. lit-ra, 1960, vol. 1.
24. *Kratkaya khimicheskaya entsiklopediya* (Abridged Chemical Encyclopedia), Knunyants, I.L., Ed., Moscow: Sovetskaya Entsiklopediya, 1961, vol. 1.
25. Becke, A.D., *J. Chem. Phys.*, 1993, vol. 98, no. 2, p. 1372; no. 7, p. 5648.
26. Lee, C., Yang, W., and Parr, R.G., *Phys. Rev.*, 1988, vol. 37, p. 785.
27. Miertus, S., Scrocco, E., and Tomasi, J., *Chem. Phys.*, 1981, vol. 55, p. 117.
28. Schmidt, M.W., Baldridge, K.K., Boatz, J.A., *et al.*, *J. Comput. Chem.*, 1993, vol. 14, no. 12, p. 1347.
29. Frisch, M.J., Trucks, G.W., Schlegel, H.B., *et al.*, *Gaussian 98, Revision A. 7.*, Pittsburgh: Gaussian, 1998.
30. Kazansky, V.B. and Senchenya, I.N., *J. Catal.*, 1989, vol. 199, p. 108.
31. Senchenya, I.N. and Kazansky, V.B., *Catal. Lett.*, 1991, vol. 8, p. 317.
32. Viruela-Martin, P., Zicovich-Wilson, C.M., and Corma, A., *J. Phys. Chem.*, 1993, vol. 97, no. 51, p. 13713.
33. Evleth, E.M., Kassab, E., Jessri, H., *et al.*, *J. Phys. Chem.*, 1996, vol. 100, no. 27, p. 11368.
34. Bell, R.P., *The Proton in Chemistry*, London: Chapman and Hall, 1973.
35. Kazanskii, V.B. and Solkan, V.N., *Kinet. Katal.*, 2000, vol. 41, no. 1, p. 46.
36. *Gaussian 94, Revision D1*, Pittsburgh: Gaussian, 1995.