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Energies of Association of Carbenium and Silylium Cations with Oxygen-Containing Molecules

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Abstract—The energies of association of $Me_nH_{3-n}X^+$ cations (n = 0–3) with molecules of oxygen-containing bases (water, methanol, dimethyl ether) were calculated by the B3LYP/6-31G(d) method. These energies decrease with an increase in the number n of methyl groups at the X atom; this trend is more pronounced for X = C, which is due to a lower degree of charge transfer in the cation from the occupied orbitals of the methyl group to the vacant orbital of X in the case of X = Si. An increase in the association energy with an increase in the number of methyl substituents at the oxygen atom is due to an increase in the energy level of lone electron pairs of oxygen upon methyl substitution. As a result, the energy gap between the electronic levels of the unoccupied orbital of the cation and orbitals of the oxygen lone electron pairs becomes narrower, which makes the interaction between the unoccupied and occupied orbitals more efficient.

Ion–molecule reactions of carbenium ions play an important role in many processes [1] and are studied both by mass-spectrometric methods in the gas phase [2] and by nontraditional nuclear-chemical methods allowing these reactions to be studied in the gas and condensed phases [3]. Silylium ions, which are analogs of carbenium ions, have been studied to a much lesser extent, and the possibility of existence of free silylium ions in condensed phases is still the matter of discussion [4–11].

Since the nuclear-chemical method allows generation of nucleogenic cations and study of their reactions in the gas phase in a wide range of pressures and also in condensed phases, it has certain advantages over the traditional mass-spectrometric methods. However, the nuclear-chemical method does not allow direct identification of the arising cations, and all the conclusions about their structure and reactivity are made on the basis of the structures and relative yields of the detected labeled neutral products of reactions of nucleogenic ions with bases (alcohols, ethers, amines). In this connection, quantum-chemical calculations of the thermochemical parameters of ion–molecule reactions, allowing the conclusions made from the experimental data to be confirmed or rejected, acquire particular importance.

At the same time, the nuclear-chemical method allows generation of both thermodynamically stable tertiary silylium ions and less stable secondary and even primary cations. Thus, prospects are opened for studying not only ion–molecule reactions of these species but also their isomerization. In this connection, it is important to know how the energy of association (adduct formation) of an ion with a molecule depends on the number of substituents in them. This problem was not studied previously.

Thus, one of important thermochemical parameters, largely governing the subsequent course of ion–molecule reactions, is the energy of association of cations with bases. This energy is spent for excitation of the vibrational degrees of freedom of the adduct and, if it exceeds the corresponding energy barrier, it can result in monomolecular decomposition of the adduct or isomerization of its structural units. Therefore, estimation of this energy furnishes important information on the possible mechanisms of formation of the products. The main differences in the heats of formation of adducts with carbenium and silylium ions are known [12–14]; with the methyl cation, this quantity significantly exceeds that characteristic of the silyl cation, but with the isostructural *tert*-butyl and trimethylsilylium cations the relationship changes [14]. Unfortunately, experimental estimates of the condensation energy for silylium ions are virtually lacking. Data are available only for the tertiary trimethylsilylium cation [15]. In this study we examined how the H/Me substitution in the cations and bases affects the energy of adduct formation, with the systems $[R^1R^2R^3X–OR^4R^5]^+$ ($R^{1–5}$ = H, Me; X = C, Si) as examples.

The results of calculating the energy of association

Table 1. Energies of association (ΔE_0, $\Delta E_0 = \Delta E_e + \Delta ZPVE$, kcal mol^{-1}) of $R^1R^2R^3HX^+$ ions with oxygen-containing bases R^4R^5O (R^{1-5} = H, Me; X = C, Si)

X	$R^1 = R^2 = R^3$ = H	$R^1 = R^1 = R^2$ = Me	R^1 = H, $R^2 = R^3$ = Me	$R^1 = R^2 = R^3$ = Me
		H_2O		
C	72.0	40.7	25.1	14.7
Si	58.5	50.4	43.4	38.1
		CH_3OH		
C	83.4	50.0	33.1	20.3
Si	66.3	56.9	49.4	43.2
		CH_3OCH_3		
C	88.9	53.9	34.6	18.6
Si	69.1	59.0	50.3	43.0

Table 2. Energies of formation (kcal mol^{-1}) of methyl cation–water complexes (ΔE_0), calculated by the B3LYP method with the cc-*pVnZ* and aug-*cc-pVnZ* (*n* = *D*, *T*, *Q*) basis sets, and the experimental value of this energy

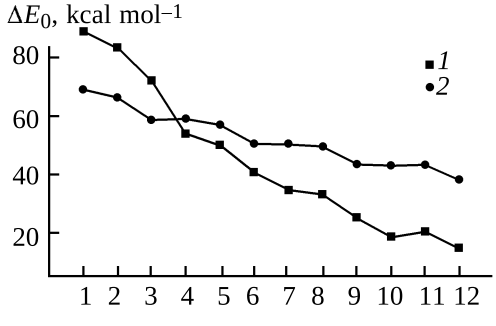
n	cc-*pVnZ*	aug-*cc-pVnZ*
D	72.6	63.5
T	66.9	63.6
Q[a]	65.2	63.8
Experiment [18]	64	

[a] Calculation for the equilibrium geometry obtained with the aug-cc-*pVTZ* basis set.

of ions with oxygen-containing molecules by the B3LYP method with the 6-31G(d) basis set are given in Table 1 and in the figure. Values are given for the zeroth vibrational level E_0 (enthalpy at 0 K); they are obtained from the calculated equilibrium energy taking into account the zero-point vibration frequencies calculated by the same method. To assess the accuracy of predicting the complexation energy by the method used, we calculated the energy of interaction of the methyl cation with a water molecule at increased size of the set of basis functions, within the framework of the correlation-consistent methodology [16, 17]. The cc-*pVnZ* set of basis functions, suggested by Dunning, allows regular improvement of the account of the electron correlation with increasing *n*. We chose the methyl cation–water system because of its small size, allowing the use of large basis sets, and because of availability of reliable experimental data for this system [18]. The calculated E_0 values converge to the experimental value of 64 kcal mol^{-1} (from above with the cc-*pVnZ* basis sets and from below with the aug-cc-*pVnZ* basis sets, with addition of diffuse functions, Table 2). The aug-cc-*pVDZ* basis set providing fairly high accuracy at relatively small size of the system was used for related but somewhat smaller systems [19]. However, application of this basis set to more complex systems studied in this work is restricted by computation resources. With the 6-31G* basis set, the energy of interaction of the methyl cation with a water molecule is overestimated by 8 kcal mol^{-1}; however, such an error in the absolute values is acceptable as far as we study trends in variation of this energy depending on substituents.

As the hydrogen atoms at the central atom X of the cations are replaced by methyl groups, the energy of complex formation with oxygen-containing molecules decreases (see figure). This trend is accounted for by interaction of the unoccupied orbital of the cation with the orbitals of the methyl group and is appreciably more pronounced with X = C. A population analysis [20] of the unoccupied p_z orbital of the X atom shows that, whereas in the SiH_3^+ and CH_3^+ ions its population is virtually zero (the orbital is unoccupied indeed), in the Me_2HX^+ ions it increases to 0.37 for X = C and 0.10 for X = Si. That is, the charge transfer to the carbon atom is appreciably stonger than to the silicon atom. This is due to the weaker overlap of the unoccupied orbital of the cation and occupied orbitals of the methyl groups, as a result of both the wider gap between their energy levels and the larger length of the Si–C bond compared to the C–C bond.

Another trend in variation of the heats of formation of the complexes depending on the number of substituents is an increase in the complex formation energy with an increase in the number of methyl groups in the oxygen-containing molecule. This trend is attri-



Energies (ΔE_0) of interaction of $Me_nH_{3-n}X^+$ with bases R^4OR^5. (*1*) X = C and (*2*) X = Si. Along the abscissa: (1) *n* = 0, R^4 = Me, R^5 = Me; (2) *n* = 0, R^4 = Me, R^5 = H; (3) *n* = 0, R^4 = H, R^5 = H; (4) *n* = 1, R^4 = Me, R^5 = Me; (5) *n* = 1, R^4 = Me, R^5 = H; (6) *n* = 1, R^4 = H, R^5 = H; (7) *n* = 2, R^4 = Me, R^5 = Me; (8) *n* = 2, R^4 = Me, R^5 = H; (9) *n* = 2, R^4 = H, R^5 = H; (1*0*) *n* = 3, R^4 = Me, R^5 = Me; (1*1*) *n* = 3, R^4 = Me, R^5 = H; (12) *n* = 3, R^4 = H, R^5 = H.

butable to an increase in the energy level of the oxygen lone electron pairs upon methyl substitution. As a result, the gap between the energy levels of the unoccupied orbital of the cation and occupied orbitals of the lone electron pairs of oxygen becomes narrower, and the stabilizing interaction between the unoccupied and occupied orbitals is enhanced [21].

The curves in the figure are drawn through 12 points, which are clearly subdivided into four groups of three points each. Within each group corresponding to the same cation $Me_nH_{3-n}X^+$, the points refer to dimethyl ether, methanol, and water. The decrease in the energy within each group is less pronounced than in going from one cation to another. This shape of the curves indicates that the methyl substitution at the X atom affects the condensation energy to a greater extent than does the substitution at the O atom.

Although a decrease in the interaction energy with increasing number of methyl groups at the X atom and with decreasing number of these groups at the O atom are observed with both carbenium and silylium ions, in the latter case the interaction energy varies to a lesser extent (less steep curve in the figure for X = Si). As a result, even for point 4 ($R^1 = R^2 = H$; $R^3 = Me$; $R^4 = R^5 = Me$), the interaction energy becomes higher with silylium ions than with carbenium ions. The difference becomes still larger for points 5–10 and then remains approximately constant for points 10–12. The lowest interaction energy is observed in the system *tert*-butyl cation–water (ΔE_0 14.7 kcal mol^{-1}, Table 1). Since the method that we used somewhat overestimates the interaction energy, it presumably does not exceed 10 kcal mol^{-1}.

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