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# Physical Chemistry

## An *ab initio* quantum-chemical study of proton addition to F-, $CH_3$-, and $CF_3$-substituted ethylene derivatives

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Protonated forms of the molecules of ethylene derivatives with the general formula $C_2X_2Y_2$ (X = Y = H (**1**), F (**2**), $CH_3$ (**3**), $CF_3$ (**4**); X = F, Y = H: *cis*- (**5**) and *trans*- (**6**)) were calculated by the *ab initio* MP2/6-31G* method with full geometry optimization. The minima and saddle points located on the potential energy surface (PES) of the protonated ethylene molecule correspond to the stationary states and transition states of proton migration, respectively. The stationary states are characterized by a nonclassical geometry of carbocations similar to that of π-complexes, whereas the transition states have a classical structure. Unlike **1**, the carbocations of molecules **2**—**6** have the classical structure. The saddle points on the PES of the ethylene derivatives correspond to the structures of the π-complex type, which are the transition states of proton migration between the C atoms of the ethylene bond. The barrier to rotation about the C—C bond depends essentially on the substituent nature.

**Key words:** *ab initio* quantum-chemical calculations, MP2 method, protonated forms of ethylene and ethylene derivatives, proton affinity, intramolecular proton migration, barriers to internal rotation.

Protonated forms of the ethylene molecule in the gas phase have been much investigated by the *ab initio* methods with inclusion of electron correlation (see, *e.g.*, Refs. 1 and 2). It was shown that such carbocations in the ground state have a nonclassical structure similar to that of a π-complex with $C_{2v}$ symmetry, in which the H atom is equidistant from the C atoms of the ethylene bond. According to calculations in the Hartree—Fock approximation, global energy minima correspond to classical carbocationic structures with $C_s$ symmetry, whereas local minima lying ~1 kcal $mol^{-1}$ higher on the energy scale correspond to nonclassical bridging forms. On the other hand, no minima corresponding to the classical carbocationic structures were located on the potential energy surface (PES) by the MP2 method with inclusion of electron correlation effects.

In this connection, it is obvious that the structure of the carbocations of ethylene derivatives can be correctly described only by using quantum-chemical methods which allow the inclusion of electron correlation. According to MP2 and QCISD calculations,[3] there are several types of saddle points on the PES of carbocation $C_2H_5^+$. They correspond either to transition between two nonclassical bridging forms with the H atom above or below the molecular plane of ethylene or to exchange of the bridging H atom with the other four H atoms. The

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activation energies of the processes are 43.5 and 6.0 kcal $mol^{-1}$, respectively.

The problem of how the substituents in the ethylene molecule affect the pathways of preferable formation of particular carbocations is of interest when studying not only the structure of these systems as intermediates, but also the model electrophilic reactions with substituted ethylenes. In this work, we calculated the PES of protonated forms of the molecules of ethylene and its derivatives $C_2X_2Y_2$ (X = Y = H (**1**), F (**2**), $CH_3$ (**3**), $CF_3$ (**4**); X = F, Y = H: *cis*- (**5**) and *trans*-form (**6**)). The effects of both electrophilic (F and $CF_3$) and weak nucleophilic ($CH_3$) substituents were considered.

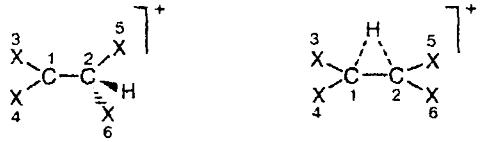
## Calculation Procedure

*Ab initio* calculations were carried out by the MP2-FC method[4] in the 6-31G* basis set using the GAUSSIAN-98 program package.[5] Stable configurations and transition states (TS) were determined by full geometry optimization using analytical gradients. The transition states for the systems under study were located using the Schlegel algorithm[6] and refined by gradient methods. The types of singular points were determined from calculations of normal vibrational frequencies. The reaction pathways from TS were found by the intrinsic reaction coordinate (IRC) method.[7] The calculations were carried out on the CRAY J-90 supercomputer (National Energy Research Supercomputer Center, Berkeley, California, USA) and SGI Power Challenger computer servers (Molecular Ecology Laboratory at the Pacific Northwest National Laboratories, Richland, Washington, USA).

## Results and Discussion

The structures of protonated forms of ethylene (**1b**) and tetrafluoroethylene (**2a**) molecules and the corresponding TS of proton migration (**1a**, **2b**) are shown in Scheme 1.

**Scheme 1**



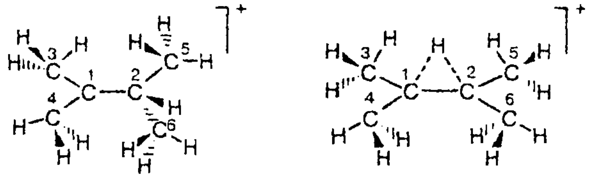
**1a, 2a** **1b, 2b**

X = H (**1**), F (**2**)

The main geometric parameters of these forms of compounds **1** and **2** are listed in Table 1. Systems **1b** and **1a** correspond to the energy minimum and to the TS of exchange of the bridging H atom with the other four H atoms of the $C_2H_5^+$ carbocation, respectively. In structure **2a**, three F atoms and both C atoms are in the same plane, whereas the fourth F atom, F(6), is above and the H atom is below this plane. Transition state **2b**, with equal C—F bond lengths, was found to be rather symmetric. The H atom is above the plane in which the C—C bond lies, while all F atoms are somewhat shifted below this plane so that the F(3)—C(1)—F(4)—C(2) dihedral angle is 173.8°. According to calculations of the neutral tetrafluoroethylene molecule in the same approximation, the equilibrium C=C and C—F bond lengths are equal (1.328 Å). Thus, protonation of molecule **2** leads to lengthening of the C—C bond by 0.228 Å. The *r*(C—F) distances in the $CF_2$ group are appreciably shortened (by 0.08 Å), whereas those in the $CF_2H$ group vary only slightly. Table 1 lists also the total energies of neutral molecules **1** and **2**, their protonated forms, and the TS of proton migration in the carbocations.

The geometries of protonated tetramethylethylene (**3a**) and the TS of proton migration between the C atoms of the ethylene bond (**3b**) are shown in Scheme 2.

**Scheme 2**

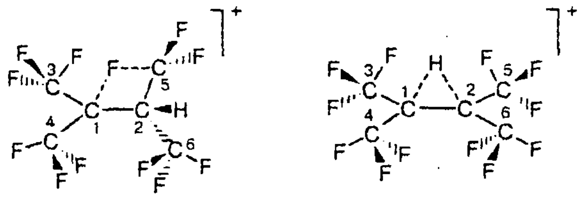


**3a** **3b**

The geometric parameters and total energies of molecule **3** and structures **3a** and **3b** are listed in Table 1. Protonation of molecule **3** leads to lengthening of the *r*(C=C) distance by 0.095 Å, shortening of the C(1)—C(3) and C(1)—C(4) bonds by 0.037 Å, and to lengthening of the C(2)—C(5) and C(2)—C(6) bonds by 0.087 and 0.010 Å, respectively.

The geometries of the protonated $(CF_3)_2C=C(CF_3)_2$ molecule (**4a**) and bridging TS of proton migration in carbocation (**4b**) are presented in Scheme 3.

**Scheme 3**



**4a** **4b**

The geometric parameters and total energies of these systems are listed in Table 1. Addition of a proton to the C(2) atom is accompanied by such an essential rearrangement of the geometry that a F atom of the $CF_3$ group appears to be simultaneously bound to two C atoms, of which one belongs to the fluoromethylene

**Table 1.** Bond lengths (*d*), bond angles (α), and total energies ($E_{tot}$) of molecules **1—6** (in numerator), their stable protonated forms **1b**, **2a—6a** (in denominator), and transition states of proton migration between the carbon atoms in carbocations **1a**, **2b—5b** (in parentheses)

| Parameter | 1 | 2 | 3 | 4 | 5 | 6 |
|---|---|---|---|---|---|---|
| Bond | *d*/Å | | | | | |
| 1—2 | 1.336 | 1.328 | 1.352 | 1.368 | 1.330 | 1.330 |
| | 1.382 | 1.553 | 1.447 | 1.536 | 1.457 | 1.462 |
| | (1.416) | (1.404) | (1.413) | (1.406) | (1.395) | (1.395) |
| 1—3 | 1.085 | 1.328 | 1.506 | 1.546 | 1.350 | 1.354 |
| | 1.088 | 1.248 | 1.469 | 1.558 | 1.255 | 1.260 |
| | (1.090) | (1.288) | (1.505) | (1.601) | (1.303) | (1.306) |
| 1—4 | 1.085 | 1.328 | 1.514 | 1.534 | 1.082 | 1.082 |
| | 1.088 | 1.251 | 1.468 | 1.550 | 1.094 | 1.094 |
| | (1.090) | (1.288) | (1.507) | (1.579) | (1.090) | (1.091) |
| 2—5 | 1.085 | 1.328 | 1.506 | 1.541 | 1.350 | 1.082 |
| | 1.088 | 1.332 | 1.593 | 1.524 | 1.355 | 1.106 |
| | (1.086) | (1.288) | (1.506) | (1.601) | (1.303) | (1.091) |
| 2—6 | 1.085 | 1.328 | 1.514 | 1.543 | 1.082 | 1.354 |
| | 1.088 | 1.345 | 1.524 | 1.539 | 1.110 | 1.361 |
| | (1.114) | (1.288) | (1.507) | (1.580) | (1.090) | (1.306) |
| 2—H | — | — | — | — | — | — |
| | 1.305 | 1.095 | 1.095 | 1.094 | 1.107 | 1.107 |
| | (1.114) | (1.380) | (1.316) | (1.326) | (1.331) | (1.331) |
| Angle | α/deg | | | | | |
| 3—1—2 | 121.7 | 123.0 | 125.4 | 125.8 | 122.0 | 119.7 |
| | 120.6 | 122.1 | 120.0 | 114.8 | 119.7 | 119.4 |
| | (122.9) | (120.9) | (122.4) | (121.7) | (121.2) | (119.2) |
| 4—1—2 | 121.7 | 123.0 | 120.0 | 124.6 | 123.2 | 125.5 |
| | 120.6 | 120.8 | 121.2 | 123.0 | 124.6 | 124.7 |
| | (120.4) | (120.9) | (121.6) | (128.8) | (121.3) | (123.2) |
| 5—2—1 | 121.7 | 123.0 | 125.4 | 125.8 | 122.0 | 125.5 |
| | 120.6 | 106.2 | 98.4 | 91.5 | 110.7 | 108.9 |
| | (116.9) | (120.9) | (122.5) | (121.7) | (121.2) | (123.2) |
| 6—2—1 | 121.7 | 123.0 | 120.0 | 122.6 | 123.2 | 119.7 |
| | 120.6 | 103.0 | 118.4 | 122.2 | 106.7 | 108.5 |
| | (107.0) | (120.9) | (121.6) | (128.8) | (121.3) | (119.2) |
| H—2—1 | — | — | — | — | — | — |
| | 58.0 | 110.7 | 110.2 | 111.3 | 108.1 | 108.2 |
| | (107.0) | (59.4) | (57.6) | (58.0) | (58.4) | (58.4) |
| Total energy | $-E_{tot}$/au | | | | | |
| | 78.2850 | 464.3409 | 234.9599 | 1423.2561 | 276.3101 | 276.3104 |
| | 78.5523 | 474.6094 | 235.2822 | 1423.4909 | 276.5679 | 276.5667 |
| | (78.5422) | (474.5575) | (235.2725) | (1423.4389) | (276.5508) | (276.5499) |

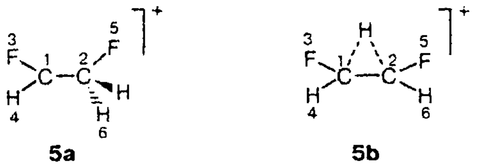
group and the other belongs to the ethylene bond. Therefore, deprotonation may cause the isomerization of the molecule as follows:

$$(CF_3)_2C=C(CF_3)_2 \rightleftarrows (CF_3)_2CF-C(CF_3)=CF_2 .$$

Schemes 4 and 5 describe the geometries of the protonated *cis*- and *trans*-isomers of 1,2-difluoroethylene (**5** and **6**, respectively) and the corresponding TS of proton migration. The calculated geometric and energy parameters of compounds **5** and **6** are listed in Table 1.

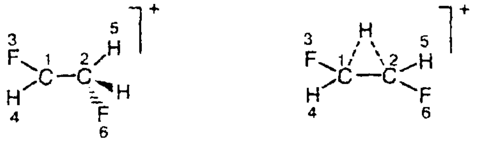
The proton affinities (*PA*) calculated in this work for molecules **1—6** (Table 2) increase as follows: **4** < **6** < **5** < **1** < **2** < **3**. Currently, only the *PA* value for ethylene (162.6 kcal $mol^{-1}$) has been determined experimentally.[8,9] Our calculations revealed that this value is 167.7 kcal $mol^{-1}$ (160.9 kcal $mol^{-1}$ with inclusion of

**Scheme 4**



**5a** **5b**

**Scheme 5**



**6a** **6b**

**Table 2.** Calculated proton affinities (*PA*) for molecules **1**—**6** and activation energies of proton migration in carbocations ($E_a$)

| Molecule | *PA* | $E_a$ |
|---|---|---|
| | kcal mol$^{-1}$ | |
| **1** | 167.7 | 6.3 |
| **2** | 168.5 | 32.4 |
| **3** | 202.3 | 6.1 |
| **4** | 147.3 | 32.5 |
| **5** | 161.8 | 10.7 |
| **6** | 160.8 | 10.5 |

zero-point energy correction, *ZPE*). For comparison, the results obtained by the configuration interaction method[2] were 172.8 kcal mol$^{-1}$ (167.9 kcal mol$^{-1}$ with inclusion of *ZPE* correction). Unfortunately, we failed to find experimental *PA* values for molecules **2**—**6** in the gas phase.

According to our calculations, the *PA* value should not be changed substantially on going from ethylene to tetrafluoroethylene (168.5 *vs.* 167.7 kcal mol$^{-1}$, respectively). This is quite surprising, since it is generally accepted that ethylene and tetrafluoroethylene play the role of nucleophilic and electrophilic agent, respectively, in the addition reactions.[10] Replacement of methyl groups for all H atoms in the ethylene molecule leads to appreciable (by 34.6 kcal mol$^{-1}$) increase in the proton affinity of the newly formed tetramethylethylene molecule, which approaches those of ethers and ketones.

On the other hand, the replacement of the trifluoromethyl groups for all H atoms in the ethylene molecule causes a decrease in the *PA* value by 20.4 kcal mol$^{-1}$. Probably, tetra(trifluoromethyl)ethylene belongs to the compounds with low proton affinities, such as saturated hydrocarbons (*cf.* *PA* = 142.7 kcal mol$^{-1}$ for ethane in the gas phase).[11] The *PA* values for *cis*- and *trans*-isomers of 1,2-difluoroethylene are lower than those for ethylene and, correspondingly, tetrafluoroethylene, which is also quite surprising.

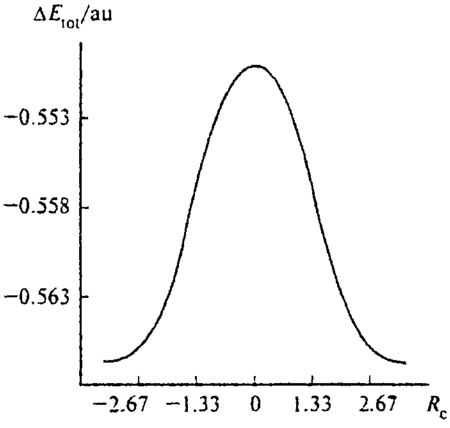


**Fig. 1.** Dependence of the relative total energy ($\Delta E_{tot}$) on the reaction coordinate ($R_c$) of proton transfer between C atoms in protonated 1,2-difluoroethylene.

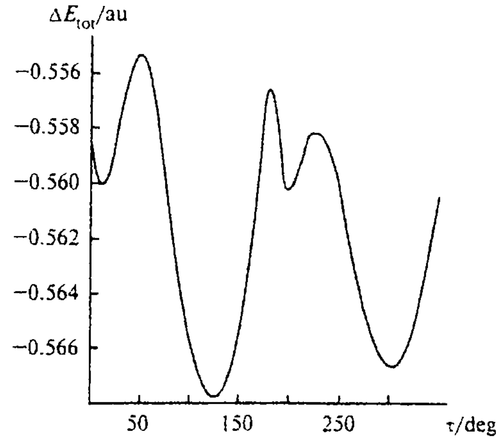


**Fig. 2.** Dependence of the relative total energy ($\Delta E_{tot}$) on the H(5)—C(2)—C(1)—F(3) dihedral angle (τ) in carbocation **6**.

The calculated activation energies of proton migration in the carbocations are also listed in Table 2. The lowest activation barriers (~6 kcal mol$^{-1}$) were obtained for the carbocations of tetra(trifluoromethyl)ethylene and unsubstituted ethylene. The activation energies of proton transfer in carbocations **2a** and **4a** exceed 30 kcal mol$^{-1}$. The plot shown in Fig. 1 describes the dependence of the total energy on the reaction coordinate of proton transfer between C atoms in the carbocation of molecule **6** (calculations by the IRC method[7]).

Rotation about the C—C bond in the carbocation of 1,2-difluoroethylene (see Scheme 5) is characterized by the dependence of the total energy on the H(5)—C(2)—C(1)—F(3) dihedral angle (Fig. 2). Three types of energy minima are observed in this curve. The deepest minimum corresponds to the *cis*-position of the atoms in the carbocation. The minimum corresponding to *trans*-position of the atoms in the carbocation lies 0.6 kcal mol$^{-1}$ higher on the energy scale. Two shallow energy minima lying 4.8 kcal mol$^{-1}$ higher than the deepest minimum correspond to a form with the bridging F atom and inequivalent distances between this atom and C atoms of the ethylene bond (1.75 Å for the C(1)—F bond and 1.48 Å for the C(2)—F bond).

Thus, the results obtained in this work suggest that the case where a proton is added at the π-bond and structure **1a** is a TS of exchange of a bridging H atom corresponds to the unsubstituted ethylene only. Protonation of ethylene derivatives with acceptor (F, $CF_3$) and weak donor ($CH_3$) substituents occurs at one of the C atoms (σ-addition) and bridging structures are the TS of proton migration in the corresponding carbocations. This conclusion is of great importance, since it does not lend support to the rather arbitrary assumption that protonation of ethylene derivatives results in the formation of π-complexes (see, *e.g.*, Refs. 12 and 13).

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