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Simulation of reactions of fluoroalkenes by quantum chemistry methods

A V Fokin, M A Landau

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Abstract. The results of simulations of the reactions and reactivity of fluoroalkenes by semiempirical and non-empirical methods of quantum chemistry are summarised. In addition to the isolated molecule approximation, methods based on the calculations of potential energy surfaces of reactions and transition states are used. The shortcomings of such calculations are analysed. The nature of chemical bonds in fluoroalkenes and the applicability of quantum chemistry methods for the calculation of their physico chemical and energy characteristics (with ionisation potentials and dipole moments as examples) are discussed. The bibliography includes 106 references.

I. Introduction

Investigation into the reaction mechanisms of fluoroalkenes is not only of theoretical significance but it is of great practical importance as well. For instance, polymerisation and copolymerisation of these compounds lead to the formation of heat-resistant fluoroplastics, the properties of which depend, in particular, on the sequence of monomers in the copolymer. Fluoroorganic compounds (including those obtained in reactions of fluoroalkenes) are widely used as lubricants, dyes, medicines, *etc*. The kinetics and mechanisms of the reactions depend on the conditions (temperature, pressure, solvent), structures and physicochemical properties of reagents, and structures of transition states. The methods of quantum chemistry can be applied to the estimation of the influence of structural and electronic factors on the course of a reaction .

As a rule, quantum chemistry calculations of potential energy surfaces for reactions and transition states give useful information, which allows a qualitative description of the reaction mechanism. However, these calculations are time-consuming and can be performed only for relatively simple systems. Furthermore, due to the approximations implied in the computational methods, the results of the calculations do not always agree with the experimental data. General principles for the construction of potential energy surfaces for reactions using quantum chemistry methods were described in detail elsewhere.[1–3] For reactions of fluoroalkenes with the simplest radicals, these calculations were performed for the first time in the early 1980's (see below). Therefore, calculations within the isolated molecule approximation are still a current topic in the theory of reactivity of alkenes since they allow one to determine the most probable site of the bond to be cleaved, or to trace changes in reactivity along certain series of molecules, in terms of different reactivity indices.

Simulation of reaction mechanisms and reactivities is closely connected with the problem of the description of chemical bonding and with physicochemical parameters of molecules. However, in quantum-chemical calculations of such characteristics as ionisation potentials, electron affinity, dipole moments, *etc*., problems as to their accuracy arise. These questions will be also discussed below.

Three chapters of our earlier monograph [4] were devoted to the quantum chemistry of fluorine-containing molecules (including fluoroalkenes). However, a number of new studies using modern computational methods have appeared, and these studies should also be summarised. Many results of these studies are based on those of earlier investigations discussed in the monograph [4], and thus we have to cite this reference often.

II. Isolated molecule approximation

The problem of the strength of the double bond in ethylene and fluoroethylenes is still far from being completely solved. According to the experimental data on bond lengths, frequencies of valence vibrations, and calculated force constants for the C=C bond, the energy of this bond should increase along the series [4]

$$H_2C=CH_2 < FHC=CH_2 < \textit{cis}\text{-}FHC=CHF < \textit{trans}\text{-}FHC=CHF \approx$$
$$\approx F_2C=CH_2 < F_2C=CHF < F_2C=CF_2. \quad (1)$$

The strength of the π-component of the C=C bond changes presumably in the same order (though, this conclusion was derived in earlier studies based on the primitive Hückel method).

According to the results of non-empirical calculations,[5] some deviations for non-symmetrical fluoroethylenes were observed. In the case of symmetrical molecules, the energy of the double bond increases along the series:

$$H_2C=CH_2 < FHC=CHF < F_2C=CF_2.$$

For non-symmetrical fluoroalkenes energy of the C=C bond changes as follows:

A V Fokin A N Nesmeyanov Institute of Organoelement Compounds, Russian Academy of Sciences, ul. Vavilova 28, 117813 Moscow, Russian Federation. Fax (7-095) 135 50 85. Tel. (7-095) 135 64 89
M A Landau N N Semenov Institute of Chemical Physics, Russian Academy of Sciences, ul. Kosygina 4, 117877 Moscow, Russian Federation. Fax (7-095) 938-21 56. Tel. (7-095) 936 17 22

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$H_2C=CH_2 \approx FHC=CH_2 > H_2C=CF_2$; $FHC=CHF > H_2C=CF_2$.

However, these conclusions[5] (as well as the results of other non-empirical and semiempirical calculations that use the optimised geometry) should be used with certain precautions (see below).

The maximum force required for the cleavage of the double bond in fluoroethylenes was taken as a criterion of its strength.[5] Non-empirical calculations within the Hartree–Fock approximation with the 5-31G basis set (modified program HONDO) were used.

The thermochemical estimation of the energy of the π-bond is based on the heats of different reactions that occur with the cleavage of this bond (chlorination, bromination, hydrobromination, polymerisation, cyclisation, *etc*.). In all cases, the heat of the corresponding reaction of tetrafluoroethylene exceeds that of ethylene by 10–16 kcal mol^{-1}.[4,6] However, further calculations of the energy of the C=C bond were performed assuming equality of the energies of the C–F bonds in CF_4 and C_2F_4, and of the C–H bonds in CH_4 and C_2H_4, which is in our opinion a very rough approximation. In one of our previous studies we attempted to explain the differences observed for the heats of reactions of ethylene and tetrafluoroethylene.[4] Quite rough estimates using the Hückel method lead to agreement between the changes in the π-bond energies for a series of fluoroethylenes and the known data on bond lengths and frequencies of stretching vibrations [series (1)]. However, this result was also obtained within rather rough approximations.

An attempt to explain the thermochemical differences in energies of the double bonds in C_2H_4 and C_2F_4 was undertaken[6] based on non-empirical calculations in the 6-31G* basis set with the use of the unrestricted Hartree–Fock (UHF) wavefunctions and Møller–Plesset second order perturbation theory (MP2). The energy required for the cleavage of the π-bond in ethylene and tetrafluoroethylene as a result of rotation of the molecule to a biradical transition state in the process of *cis–trans*-isomerisation was calculated. Thermochemical estimates of the bond energy were confirmed, and weakening of this bond in C_2F_4 compared to C_2H_4 was explained by a 'planarisation' of two CF_2 groups (since the carbon atoms in these groups in the biradical transition state are 'pyramidised' to a great extent).

An approach to estimating the energy of the π-bond as the difference between the energies of a triplet *twist*-biradical and a planar alkene[6] does not take into account changes in the energy of C=C, C–F, and C–H σ-bonds in the rotation. Therefore, we suppose that the data on bond lengths and frequencies of stretching vibrations of the double bond in alkenes [series (1)] describe more adequately the order of changes in the energy of the C=C π-bond in fluoroalkenes (since, in general, substitution hardly affects the length of the σ-bond).

The rates of different reactions of fluoroalkenes that occur with cleavage of the C=C π-bond increase along the series (1). This refers to the reactions with nucleophilic reagents[4,7] and to some radical reactions. Tetrafluoroethylene reacts with alcohols even at room temperature, whereas an analogous reaction for ethylene is impossible,[8–10] which is explained only by kinetic rather than thermodynamic factors. For instance, at 25 °C the equilibrium for the reaction of ethylene is almost totally shifted towards etherification.[11]

The reactions with nucleophilic reagents should proceed more easily the lower the energy of the lowest unoccupied molecular orbital (LUMO), *i.e*. the higher the affinity of the molecule for the electron. According to results of CNDO and INDO calculations,[12] the LUMO of fluoroethylenes is an antibonding π-orbital of ethylene perturbed by fluorine atoms. The values of E^n for ethylene and tetrafluoroethylene are 5.36 eV and 3.72 eV (CNDO) and 5.91 eV and 4.20 eV (INDO), respectively. These values clearly explain why tetrafluoroethylene reacts much more easily with nucleophiles than ethylene.†

Of course, the values given are relative, but they agree qualitatively with the results of calculations by different modifications of non-empirical methods that use basis sets with only *s*- and *p*-orbitals. However, an introduction of *d*-orbitals into the basis leads to opposite results, which are in agreement with rather scarce and approximate experimental data (see below). A decrease in the calculated values of E^n along the series $F_2C=CF_2 > F_2C=CFCF_3 > F_2C=C(CF_3)_2$ is also in agreement with the experimentally observed increase in the reactivity of the above-mentioned molecules in reactions with nucleophiles.[13]

Populations on carbon atoms and overlapping populations of the C=C π-bond on lower occupied π-orbitals formed by conjugation of lone pairs on the fluorine atom with the π-bonding orbital of ethylene are negligibly small compared to the population of the highest occupied π-orbital formed primarily by the π-orbital of ethylene (see Ref. 4 in which the results of the *ab initio* calculations are given).

In reactions with alcohols, thiols, and amines, tetrafluoroethylene gives only addition products.[7,13] Together with addition products (2), perfluoropropylene also gives products of vinylic (3) and allylic (4) substitution.

$$F_2C{=}CFCF_3 + ROH \longrightarrow \begin{cases} ROCF_2{-}CFHCF_3 & (2) \\ ROCF{=}CFCF_3 + HF & (3) \\ CF_2{=}CFCF_2OR + HF & (4) \end{cases}$$

In the case of perfluoroisobutylene, only reactions (2) and (3) occurred.[6,13,14] Vinylic substitutions

$$F_2C{=}CFCl + NaSC_2H_5 \longrightarrow C_2H_5SFC{=}CFCl + NaF$$

and

$$F_2C{=}CFCl + PhLi \longrightarrow PhFC{=}CFCl + LiF$$

could be accomplished in the case of chlorotrifluoroethylene[4] and perfluoro-*tert*-butylethylene.[15] In the latter, only the fluorine atom *trans* to the $(CF_3)_3$ group undergoes substitution in reactions with carbonylmetallates. However, in the case of $(CF_3)_3CCF=CFX$ (X = Cl or Br), in the reaction with carbonylmetallates, the substitution products are not formed.[15] Other examples of analogous reactions with fluoroalkenes are given elsewhere.[4,14–17]

Products of vinylic substitution, together with addition products, are also formed in reactions of 1,2-dibromo-1,2-difluoroethylene, tribromofluoroethylene, and bromotrifluoroethylene with alkoxides.[18,19] In the case of $F_2C=CFBr$, the main site of attack by a nucleophile is the carbon atom of the CF_2 group (the yield of the addition products and the products of substitution of a fluorine atom in the CF_2 group by OR is 80%–94%). Oligomers or polymers and trifluoroethylene are also formed as by-products (less than 0.5%).

The above-mentioned features of reactions of perfluoropropylene and trifluorochloroethylene were interpreted in terms of the results of quantum-chemical calculations by the CNDO method.[20–22] Allylic substitution in the case of perfluoropropylene occurs because, according to the results of the calculation, the carbon atom of the trifluoromethyl group carries the maximum positive charge. However, due to great steric hindrances, reaction (2) appears to be preferable (attack at the CF_2 group, which also carries a relatively large positive charge). In the case of perfluoroisobutylene, the reaction (4) is impossible due to steric hindrance. The same holds for the reaction of perfluoropropylene with bulky thiol molecules, which follow only pathways (2) and (3).[13]

† It should be noted that many features of reactions with fluoroethylenes and of changes in their reactivity have already been rationalised in the first quantum-chemical studies using the primitive Hückel method (for more details, see Ref. 4).

Vinylic substitution (3) can be explained by a substantial increase in the polarity of the C–F bond of the CF_2 group on going from tetrafluoroethylene to perfluoroisobutylene and chlorotrifluoroethylene.[20] Despite the fact that the negative charge on the fluorine atom is almost constant for all the four molecules considered, the positive charge on the carbon atom of the CF_2 group in perfluoropropylene, perfluoroisobutylene, and trifluorochloroethylene is substantially higher than in tetrafluoroethylene (Table 1).

In the case of phosphorus fluorides for which substitution of the fluorine atoms is typical, the P–F bond is even more polar according to calculations by the CNDO method.[4, 22, 24] Vinylic substitution in fluoroethylenes for which experimental data are lacking, has been analysed based on the bond polarity criterion.[22]

According to the polarity criterion for the C–F bond, the probability of vinylic substitution is low in monofluoroethylene and both (*cis* and *trans*) 1,2-difluoroethylenes: the difference between the charges on the carbon and fluorine atoms Δq (calculated by the CNDO method) is substantially smaller than in tetrafluoroethylene. However, these reactions are highly probable for 1,1-difluoroethylene and trifluoroethylene: the difference in charges on the carbon and fluorine atoms for these molecules is more than 0.55 (as for perfluoropropylene, perfluoroisobutylene, and chlorotrifluoroethylene), which is larger than the corresponding value for tetrafluoroethylene (0.48, Table 1).

Similar results were obtained in *ab initio* calculations, which are summarised in Table 1, *viz*. atomic charges and Δq values calculated from the data on populations of the corresponding atomic orbitals.[23] Values of Δq for 1,1-di- and tri-fluoroethylenes are also substantially larger than for other members of the series.

Similar results were obtained by the INDO method.[22]

Charge distributions in non-symmetrical fluoroethylenes indicate [4, 12] that the addition of hydrogen halides to these molecules should obey the Markownikoff rule, which is in agreement with the experimental data.[7, 13] The results of the corresponding semiempirical (CNDO, INDO) and non-empirical calculations [4] also support this conclusion (see also charges of the carbon atoms given in Ref. 5). In reactions with alcohols and thiols, the $RO^-(RS^-)$ group also adds to the carbon atom, which according to calculations [12] has a relatively high positive charge. A similar conclusion was derived [4, 12, 20] from calculations of 1,1-dichloro-2,2-difluoroethylene, chlorotrifluoroethylene, perfluoropropylene, and perfluoroisobutylene which is confirmed by the experimental data. The orientation of borane addition to monofluoroethylene according to calculations by the MNDO method,[25] is also in accordance with the experimental data (see also charges of fluoroalkenes calculated by the CNDO method [26]).

Generally, in vinylic substitution in non-symmetrical haloethylenes, nucleophilic attack can occur at both carbon atoms of the double bond (see, for example, Ref. 15). The probability of such attack should increase with a decrease in the charge difference between the two carbon atoms. If a molecule contains a CFX group (X = Cl, Br), substitution of both F and X is possible.[15] This is observed, for example, in the reaction of β-chloro-α,β-difluorostyrene with phenyllithium and $KFe(CO)_2Cp$.[15] The difference in charges on the carbon atoms of the double bond is small (0.171, calculated by the AM1 method).[27] Despite the fact that the charge of the carbon atom on the PhFC group is greater than that of the CFCl group, a nucleophile attacks only the =CFCl fragment (presumably, due to steric hindrances because of the presence of the benzene ring in PhFC=). A competitive substitution of both fluorine and chlorine atoms occurs.

Unfortunately, the charges on the F and Cl atoms were not given in Ref. 27, and thus it is impossible to estimate the probabilities of the two reactions in terms of polarity of the C–X bond. Presumably, the substitution of the F atom is more probable. This assumption is in agreement with the results of calculations for other molecules (chlorotrifluoroethylene, in particular [20]) and with the above-mentioned data on reactions of tribromofluoroethylene.[19] In addition, we believe that $KFe(CO)_2Cp$ or $Re(CO)_5$, in general, cannot be considered as classical nucleophiles. In the course of the reaction, intermediate complexes can be formed through dative bonds between the Fe (Re) atom and the π-orbital of alkene as well as by donor–acceptor bonds between CO and the vinyl group.

A detailed study of electrochemically activated reactions of nucleophilic substitution of polyfluorinated vinyl halides was performed,[27, 28] and quantum-chemical calculations for the nine alkenes considered, four fluorinated butadienes, and fluorinated acetylenes were accomplished.[27] The semiempirical AM1 method with full geometry optimisation was used. Energies of frontier π-orbitals of the molecules studied and charges on the vinylic carbon atoms were determined. Other parameters (in particular, charges on halogen atoms, interatomic distances, bond angles) were not given in Ref. 27. However, certain problems in the interpretation of the results of quantum-chemical calculations that use optimised geometry may arise (see below). The electron acts as the simplest nucleophile. In the case of the formation of rather stable radical-anions upon interaction of a haloalkene with an electron [for instance, $(RFC=CFX)^{\bullet -}$], the nucleophilic substitution is a 'multi-step' process.[27] If no radical-anions are formed, the nucleophilic substitution is a 'one-step' process.

Changes in frontier π-orbitals of ethylene upon substitution of halogens for hydrogen were thoroughly analysed.[27] Energetic, spatial, and kinetic factors were considered.

The energy of the π-orbitals of the double C=C bond perturbed by halogen atoms depends both on conjugation of a lone *p*-electron pair of the halogen with the electrons of the π-bond

Table 1. Charges on the carbon (q_C) and the fluorine (q_F) atoms in fluoroalkenes calculated by the CNDO [22] (I) and *ab initio* [23] (II) methods and the difference between the charges of C and F (Δq).

Molecule	q_C		q_F		Δq	
	I	II	I	II	I	II
$\underline{F}HC=CH_2$	+0.209	+0.263	−0.186	−0.361	0.395	0.624
cis-$\underline{F}HC=CH\underline{F}$	+0.143	+0.101	−0.166	−0.335	0.309	0.436
trans-$\underline{F}HC=CH\underline{F}$	+0.141	−0.054	−0.169	−0.335	0.310	0.281
$\underline{F}_2C=C\underline{F}_2$	+0.317	+0.534	−0.159	−0.274	0.476	0.808
$\underline{F}_2C=C\underline{Cl}F$	+0.398	–	−0.159 (−0.165)	–	0.557 (0.563)	–
$\underline{F}_2C=CFCF_3$	+0.418	–	−0.163 (−0.158)	–	0.581 (0.576)	–
$\underline{F}_2C=C(CF_3)_2$	+0.520	–	−0.164	–	0.684	–
$\underline{F}_2C=CH_2$	+0.448	+0.654	−0.192	−0.313	0.640	0.967
$\underline{F}_2C=CFH$	+0.379	+0.600	−0.173(−0.174)	−0.294 (−0.291)	0.552 (0.553)	0.894 (0.891)

Note. The fluorine atoms for which values of q_F are given are underlined. Values of q_F are given for the fluorine atom in the *cis*- (no parentheses) and *trans*- (in parentheses) positions to the fluorine atom of the CFX group. In calculations on chlorotrifluoroethylene, vacant 3*d*-orbitals of the Cl atom were included into the basis set.

and on the inductive influence of the halogen atoms. Both these factors should favour easier reduction of alkenes in the series $C=CBr < C=CCl < C=CF$.[27] The spatial factor is interrelated with the orbital size of the halogen atom and acts in the opposite direction to the energetic factor: $C=CF < C=CCl < C=CBr$.

The kinetic factor depends on the rate of fragmentation of the radical-anion that is formed in the first stage of the process. The influence of the kinetic factor changes in the same order as that of the spatial factor (for details, see Ref. 27).

The vinylic carbon atom of the CF_2(CFCl, CFH) group has the greatest (in absolute value) charge in *tert*-$C_4F_9CF=CF_2$, *tert*-$C_4F_9CF=CFH$, and *tert*-$C_4F_9CF=CFCl$,[27] though in the two latter cases, the difference in charges on the carbon atoms of the double bond is small, and the charge on the carbon atom of the CFCl group is close to zero.

In the case of trifluorostyrene, a nucleophilic attack at the CF_2 group for which $q_C = +0.112$ is preferable; for the PhFC group, $q_C = +0.046$. Due to such a small difference in charges, an attack at both carbon atoms of the double bond is to some extent probable. In contrast, the carbon atom of the PhFC group in $PhFC=CHF$ and $PhFC=CFCl$ carries the positive charge whilst another carbon atom of the double bond carries a small negative charge.[27]

It should be noted meanwhile that according to our results[29] obtained by spectral methods (^{19}F NMR, IR, UV), a mixture of cyclic dimers is formed as a result of γ-irradiation of planar trifluorostyrene (which is rather typical of fluoroalkenes). On the other hand, γ-irradiation of non-planar *trans*-difluorostilbene adsorbed on aluminosilicate leads to a trimer[30] formed by elimination of hydrogen atoms of the benzene rings of the monomer, the double bond being retained (for details, see Refs 4, 29, and 30). Preliminary experiments carried out under identical conditions demonstrated that the trimerisation with retention of the double bond is specific for *trans*-difluorostilbene and is not due to differences in experimental conditions for the two monomers.

A linear correlation was established between the calculated energies E^n of LUMOs for compounds studied and experimental electrochemical potentials.[27] Electrochemical reduction becomes easier with a decrease in E^n,[27] but no parameters and statistical criteria for the equation derived were given.

Seventeen perchlorofluoroalkenes were calculated using the MNDO method in combination with the perturbation theory.[31] Changes in energy in the formation of a bond between an alkene (*s*) and a nucleophile (*t*) in the interaction of these alkenes with CH_3OLi in ether (ΔE) were calculated:

$$\Delta E = \frac{q_s q_t}{R_{st}\varepsilon} + 2\sum \frac{(c_s c_t s t)^2}{E_H - E_L}, \qquad (5)$$

where q_s and q_t are charges on *s* and *t* atoms in isolated molecules, $\varepsilon = 4.34$ is the dielectric constant, $R_{st} = 1.7$ Å is the distance between the *s* and *t* atoms in the transition state, c_s and c_t are the coefficients of AOs of these atoms in frontier MOs, and E_H and E_L are the energies of the frontier orbitals of the nucleophile and alkene, respectively. The first term in equation (5) accounts for the contribution of electrostatic interactions, the second corresponds to perturbation of the covalent bonds.

For all of the compounds studied, the second terms in equation (5) for both carbon atoms of the double bond are approximately equal, and thus a nucleophile attacks the atom with the maximum positive charge.

However, there are several exceptions to this rule. For example, molecules with an allylic chlorine atom are more reactive than the corresponding perfluoro analogues, and a nucleophile attacks the carbon atom of the double bond most remote from the chlorine atom even if this atom carries a lower positive charge than the another carbon atom of the double bond. This was rationalised by the fact that the allylic chlorine atom stabilises the transition state and decreases the activation energy of the reaction.

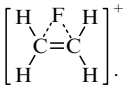
According to the calculated ΔE values, it was established that the reactivity of the compounds studied with respect to hard nucleophiles (to CH_3OLi, in particular) decreases along the series $CF_2=CFR_F > CF_2=CF_2 > R_FCF=CFCl > R_FCF=CClR'_F > R_FCF=CFR'_F > R_FCF=CCl_2$ (where R_F is a perfluoroalkyl radical), which is in accordance with the known experimental data.

The results obtained allowed the prediction of the site of nucleophilic attack in an alkene molecules. For instance, CH_3OLi should attack the carbon atom of the CF_2 group in $CF_2=CFCF_3$ ($\Delta E = -23.01$ kcal mol^{-1} as compared to -6.78 kcal mol^{-1} for the carbon atom of the $CFCF_3$ group involved in the formation of the double bond);[31] this coincides with the experimental data.[13] However, in $R_FCF=CCl_2$, the values of ΔE are similar for both carbon atoms, and the direction of the reaction is determined by the coefficient of the AO in the frontier MO: a nucleophile attacks the carbon atom with higher c_s (in this case, it is the carbon atom of the CCl_2 group).

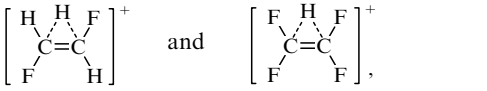
It was pointed out [31] that the direction of the reactions studied is determined not only by the rate of the bimolecular stage leading to the carbanion but also by the relative stability of the intermediate products. The enthalpies of formation of the possible intermediate products were calculated. For instance, it was found that in the reaction of $CF_3CF=CFCFCl_2$ with OH^-, the anion $(CF_3-CF(OH)-CF-CFCl_2)^-$ is more stable than $[CF_3-CF-CF(OH)-CFCl_2]^-$. Calculations of intermediate products [31] lead to better agreement with the experimental data than calculations by perturbation theory.

The acceptor strength of perchlorofluoroalkyl radicals (estimated from charges of the carbon atoms of the double bond linked to them) increases along the series $CF_3 < CF_2Cl < CFCl_2 < CCl_3$ (for details, see Ref. 31).

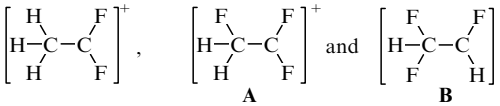
The structures of the cations formed by protonation of fluoroethylenes were analysed [5] using non-empirical calculations with atomic Hartree–Fock functions in the 5-31G basis set). In the case of monofluoroethylenes, the following symmetrical carbocation should be formed:[5]



Protonation of *trans*-1,2-difluoroethylene and tetrafluoroethylene also results in the formation of symmetrical π-complexes with retention of the covalent C–F bonds



1,1-difluoroethylene and trifluoroethylene should form σ-complexes on protonation [5]



A **B**

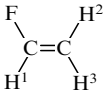
and the configuration **A** is more favourable than **B**. π-Complexes are much more stable than σ-complexes.[5]

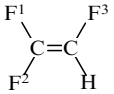
Other examples of similar studies are given elsewhere.[4] A problem arises in the choice of the molecular geometry. In non-empirical and semiempirical calculations, the energy minimisation procedure is often applied, and further calculations of quantum-chemical characteristics are performed for the structure, which corresponds to the global energy minimum. However, noticeable deviations between the calculated and experimental geometrical parameters for the gas phase are often observed. For example, for fluoroethylenes, the difference between the experimental and calculated bond lengths does not exceed 0.03 Å, which can hardly affect substantially the calculated physicochemical parameters. Only for calculations by the MNDO method do the calculated bond lengths deviate strongly from the experimental ones. How-

ever, the difference between the calculated and experimental bond angles in some cases reaches 4°, which inevitably introduces errors in the values of some physicochemical parameters and quantum-chemical indices (dipole moments, ionisation potentials, *etc.*).[4] For instance, changes in ionisation potentials for the series of fluoroethylenes obtained by the LCAO SCF *ab initio* calculations in the DZ basis not only disagree with the experimental data, but do not reflect any regularity in contrast to the results of semi-empirical calculations (EHT, CNDO, INDO), which use the experimental molecular geometry (see Refs 4 and 12).‡

The same problem was discussed in another study.[32] It was shown that in the case of full geometry optimisation by the MNDO and *ab initio* methods, not only the calculated bond angles, but also the C=C and C–F bond lengths differ considerably from the experimental values.

Recently,[33] enthalpies of formation, moments of inertia, vibration frequencies, and geometrical parameters for more than 100 fluorinated hydrocarbons and radicals containing one or two carbon atoms were calculated using the non-empirical BAC-MP4 method (fourth order Møller–Plesset perturbation theory corrected for additivity of bonds). It was found that the bond angles coincide with the experimental data within 1° on average. However, as can be seen from the tables given in Ref. 33, this is not quite true for fluoroethylenes, especially for non-symmetrical ones. In some cases, as well as in the studies mentioned above, deviations from the experimental data reach 4°, for example,





Angle	Value of angle /deg.		Angle	Value of angle /deg.	
	calculation [33]	experiment [4]		calculation [33]	experiment [4]
CCF	122.4	120.98	CCF^1	125.4	125.43
CCH^1	125.7	127.70	CCF^3	120.6	118.81
CCH^3	119.8	121.41	CCH	123.4	127.20
CCH^2	121.5	123.93			

The problems discussed in Ref. 33 lie somewhat beyond the objectives of the present review (though the authors point to the need for kinetic studies). In the above-mentioned study, neither data on the energy of molecular orbitals, nor populations of atomic orbitals and atomic charges were given, and the mechanisms of the reaction with participation of the compounds studied were not considered.

III. Potential energy surfaces of reactions and structure of transition states

First studies devoted to calculations of potential energy surfaces of reactions with the participation of fluoroethylenes appeared in 1980.[34, 35] The unrestricted Hartree–Fock method with split valence basis set 4-31G was used. In particular, a mechanism of reaction of monofluoroethylene with atomic hydrogen was discussed.[34] Potential energy surfaces of the following reactions were studied by non-empirical MO LCAO methods:

$$H_2CCH_2F^{\bullet} \longrightarrow H_2C{=}CHF + H^{\bullet},$$
$$H_2C{=}CHF + H^{\bullet} \longrightarrow H_2CCH_2F^{\bullet} \qquad (6)$$

as was of a similar reaction of ethylene.[35] The main contribution to the potential barrier (E) of reaction (6) equal to 5.6 kcal mol^{-1} arises from deformation of the H_2CCHF segment in the transition state (4.5 kcal mol^{-1}); the rest (1.1 kcal mol^{-1}) is due to interactions of the $FHC{=}CH_2$ fragment with H. The potential barrier of reaction (6) exceeds by 3.3 kcal mol^{-1} that of the reaction

$$H_2CCH_2 + H^{\bullet} \longrightarrow H_2CCH_3^{\bullet}.$$

The lifetime of $H_2CCH_2F^{\bullet}$ is relatively great (10^{-9} s). If the process has adiabatic character, the energy E converts to the translation energy of the reaction products [35] (see also Ref. 4).

The studies [34, 35] were based on general principles of analysis of potential energy surfaces for radical reactions developed by Nagase, Morokuma, and Kern.[34, 36, 37]

Reactions of atomic hydrogen with 1,1-difluoroethylene and monofluoroacetylene were studied in detail.[38] An *ab initio* method within the unrestricted Hartree–Fock theory (modified version of Gaussian 70) was used. It was demonstrated that in both cases the preferential site for a nucleophilic attack is the carbon atom not bonded with the fluorine atom. The potential barrier to the reaction of 1,1-difluoroethylene (4.1 kcal mol^{-1}) [38] is higher than that of ethylene (2.2 kcal mol^{-1}).[34]

Potential energy surfaces, structures of transition states for reactions of fluoroethylenes with alkyl radicals and heteroradicals as well as the regioselectivity of alkyl radicals in reactions with non-symmetrical fluoroethylenes were discussed in a number of papers [39–44] (see also Ref. 4). The extended Hückel method (EHT) was used.[39, 40] The conclusions derived in Refs 39 and 40 are not always correct from our viewpoint. For instance, attempts to analyse the mechanisms of the reactions studied of ethylene and fluoroethylenes [40] with $CH_3^{\bullet}$ and $CF_3^{\bullet}$ using different correlations between the experimental activation energy and the calculated quantum-chemical indices do not meet any criteria of mathematical statistics.§

A more thorough analysis of the mechanisms of radical reactions was performed using the concept of 'phility' of free radicals in reactions of addition to alkenes.[41–44] This concept is based on a hypothesis [45] of a parallelism between the direction of the charge transfer and localisation of the bonds formed and cleaved and on an assumption [46] that the potential barrier to a reaction depends on the charge transfer stage and that the strongest charge transfer in a transition state corresponds to the most preferable reaction pathway. A hypothesis [47] stating that the interaction of centres with the maximum electron density on frontier orbitals of the reagents (the HOMO of the alkene and the orbital with the unpaired electron of the radical for the stage of charge transfer from alkene to radical; and the LUMO of the alkene and the same orbital of the radical for the stage of charge transfer from the radical to the alkene) is the most preferable, is also implied.

Depending on the substrate, a radical can act as a nucleophile and an electrophile, and can exhibit ambiphilic properties (in the case that the charge transferred from the orbital of the radical occupied by one electron to the lowest unoccupied π-orbital of the alkene is close to the charge transferred in the opposite direction from the highest occupied π-orbital of the alkene to the radical orbital). In general, certain radicals and an alkene can act as nucleophiles and electrophiles (donors and acceptors) simultaneously donating and accepting electrons. The 'phility' is determined by the predominating process.

The 'phility' concept,[41] first, allows one to determine the most reactive centre of a non-symmetrical alkene molecule; second, to predict changes in the reactivity of a given radical with different alkenes or a given alkene with different radicals; and third, to estimate the preferred direction of charge transfer in the system (from the alkene to the radical or, conversely, from the radical to the alkene).

To determine the reaction rate constants, the stabilisation energy method,[1] the concept of a 'quasi-π-electron system' of the

‡ Unfortunately, there are no published data on the orbital populations and all atomic charges of fluoroalkenes calculated *ab initio* with a more complete basis set.

§ Plots of dependences of $(E-E_0)_{exp}$ on the theoretical value $(E-E_0)_{theor}$, the sum of contributions of charge transfer, and contributions of exchange repulsion were discussed [40] (E and E_0 are activation energies of fluoroethylene and ethylene, respectively). However, only four or five experimental points (equal to the number of molecules studied) were used in data processing, and strong deviations from the theoretical line were observed. No statistical criteria, except for the correlation coefficient, for the dependences obtained were given [40] (for details, see Ref. 4).

transition state (*i.e.* the electron system that comprises π-systems of the initial molecules),[48] and a one-electron method of perturbation theory within the frontier orbitals approximation have been used.[42,43]

Reactions of ethylene and fluoroethylene with six alkyl and halogenoalkyl radicals ($CH_3^{\bullet}$, $CH_2F^{\bullet}$, $CHF_2^{\bullet}$, $CF_3^{\bullet}$, $C_2F_5^{\bullet}$, and $CCl_3^{\bullet}$) and four heteroradicals [$PH_2^{\bullet}$, $P(CH_3)_2^{\bullet}$, $SH^{\bullet}$, $S(CH_3)_2^{\bullet}$] were discussed.[42,43] An analogous approach was also used for the qualitative prediction of the direction of radical substitution reactions in an aromatic ring[49] and for a investigation of the reactions of fluoroethylene copolymerisation.[50]

The results obtained[41–44,49,50] reflect adequately the experimental data on reaction mechanisms and reactivities of the molecules studied. Generalisation of these results has led to the development of a model of intermolecular ambivalence in organic reactions.[51]

After publication of the monograph,[4] several studies devoted to quantum-chemical calculations of potential energy surfaces for reactions of fluoroalkenes appeared. Hydrogen migration in the monofluoroethylene molecule was studied[52] *ab initio* on a Hartree–Fock atomic orbital basis using perturbation theory. It was shown that a local minimum on the energy surface does not correspond to the singlet state of the rearrangement product.

$$H_2CCHF \longrightarrow HCCH_2F\,.$$

The problems of accounting for the correlation effects that arise when determining the geometry of transition states are the same as in calculations of the ground state structures of molecules. The authors of a study[53] of addition reactions of $H^{\bullet}$, $OH^{\bullet}$, $NH_2^{\bullet}$, and $CH_3^{\bullet}$ radicals to mono- and 1,1-di-fluoroethylenes using non-empirical calculations (up to MP4/6-31G**) came to a conclusion on the necessity of accounting for the electron correlation when determining the structures of transition states for reactions of fluoroalkenes with electrophilic radicals. The importance of accounting for the electron correlations in quantum-chemical calculations of reactions of fluoroethylenes with radicals was also discussed in other studies.[52,54,55] In all these studies, different modifications of the *ab initio* method were used [Hartree–Fock atomic orbitals MP2–MP4/DZ + P; 6-31G**; 6-311G**; 6-311 + G(2*d*,*p*); 6-311 + G(3*df*,2*p*), *etc*.].

The relative reactivity of the above-mentioned radicals in reactions with monofluoroethylene and difluoroethylene obtained from calculations[53] is in agreement with the experimental data. However, the regioselectivity of $OH^{\bullet}$ and $NH_2^{\bullet}$ radicals is very 'sensitive' to the level of theoretical calculations, and an increase in this level up to MP4/6-31G** may lead to a contradiction with the experimental data (an attack at the carbon atom of the FHC and F_2C groups according to calculations rather than of the H_2C group according to experiment).[53]

Non-empirical calculations of potential energy surfaces of addition reactions of $H^{\bullet}$, $CH_3^{\bullet}$, $CH_2OH^{\bullet}$, $CH_2CN^{\bullet}$, and *tert*-$C_4H_9^{\bullet}$ radicals to alkenes $H_2C{=}CHX$ (X = H, CH_3, NH_2, OH, F, SiH_3, Cl, CN, CHO, NO_2) were performed.[54,55] A correlation between the potential barrier and the reaction enthalpy was established ($R^2 = 0.973$). However, besides the correlation coefficient, no other statistical criteria were used for the dependence obtained, which does not allow one to judge its correctness. Problems of the statistical significance of correlation equations were analysed in detail elsewhere.[56–59]

The methyl radical does not manifest nucleophilic properties in reactions with the alkenes studied (X = F, H, OH, CH_3, SiH_3, and NH_2) and acts as an electron acceptor (*i.e.* the charge is transferred from the alkene to $CH_3^{\bullet}$).[54] In the case where X = Cl, according to the results of calculations, charge transfer does not occur at all; for X = CHO, NO_2, and CN, methyl acts as an electron donor (*i.e.* exhibits nucleophilic properties: the charge is transferred from $CH_3^{\bullet}$ to the alkene).

Electron-acceptor groups increase the reactivity of alkenes due to an increase in the exothermicity of the reaction rather than the polar character of the transition state.[54]

The stability of fluorine-containing cations including $H_2C{=}CHFCH_3^+$ and $H_2C{=}CHCHF^+$ was studied by the *ab initio* SCF method in the 6-31G basis set (Gaussian 82 programme).[60] An analysis of singlet and triplet transition structures in the process of trifluoroethylene formation in the photolysis of 2,2,2-trifluorodiazoethane was performed[61] using the *ab initio* method at the QCISD(T)-FC/6-311(2*s*,2*p*)/MP2-FC/6-31G** theory level.

The results of non-empirical calculations for $C_3H_2F^+$, $C_3HF_2^+$, and $C_3F_3^+$ ions are given elsewhere[62] (SCF, Hartree–Fock, 6-311G).

Potential energy surfaces for molecules of X_2F_4 type (X = C, Si, Ge, Sn, and Pb) were studied in detail using *ab initio* methods (RHF and UHF, DZ and DZd basis sets).[63] In particular, it was established that the planar structure of C_2F_4 corresponds to the energy minimum. Similar energy minima were found for ground states of Si_2F_4, Ge_2F_4, Sn_2F_4, and for a singlet excited state of Pb_2F_4. It was shown that a biradical triplet particle $F_2X^{\bullet}{-}X^{\bullet}F_2$ has higher energy than the singlet particle in the ground state.

IV. Quantum-chemical calculations of the physicochemical parameters of fluoroalkenes

Different aspects of the quantum chemistry of fluoroalkenes, such as the nature of the chemical bonds therein, relative stability of geometrical isomers, and calculations of physicochemical parameters, have been discussed in detail previously.[4] Problems arising from the interpretation of the results of calculations and from calculations of certain parameters (ionisation potentials, dipole moments, different energy characteristics, magnetic shielding constants of ^{19}F and ^{13}C nuclei, and so on) have been also analysed. Most of these parameters affect the character and quantitative characteristics of reactions of fluoroalkenes and thus they are closely connected with the objectives of the current review. The results of quantum-chemical calculations of physicochemical parameters of fluoroalkenes obtained in the 1990's have been analysed in another review.[64] Here, we will discuss in brief only the problems that concern the reactivity and mechanisms of reactions of compounds of this class.

Difficulties arising from the calculations of geometrical parameters of molecules have already been mentioned. Non-empirical calculations of neutral molecules and dications of type $C_2X_2Y_2^{2+}$ were performed[65] in the 3-21G*(*d*) basis set using the Gaussian 88 programme. In particular, it was shown that dication $C_2F_4^{2+}$ has a planar configuration in the ground state in contrast to the *twist*-structure of $C_2H_2^{2+}$. Serious problems also arise in the calculation of the ionisation potentials and dipole moments of molecules.

1. First ionisation potentials; electron affinity

The first ionisation potential *I*, which corresponds to detachment of an electron from the HOMO, is the most interesting for chemists: the value of *I* to some extent correlates with the reactivity of a molecule in reactions with electrophilic reagents. Linear correlations between the logarithms of rate constants of certain reactions and *I* values are often found for narrow subsets of closely related compounds.

In order to estimate *I*, the difference between the energies of the ion formed and the initial molecule $\Delta E'$ has to be calculated.

According to Koopmans theorem,[66] if wavefunctions are not changed after detachment of an electron from certain MO, the corresponding ionisation potential is equal to the energy of this orbital E_i. This implies that the difference between the correlation energies of the ion and molecule ΔE_c is equal to the reorganisation energy ΔE_r taken with the opposite sign,[67] since

$$I + E_i = \Delta E_c + \Delta E_r\,,$$

where ΔE_r is the difference between the energy of the HOMO calculated in the optimum modification of the Hartree–Fock method and the ionisation potential.[68]

Usually, ionisation potentials I calculated according to Koopmans theorem using different semiempirical and non-empirical methods of the self-consistent field (SCF) approach exceed the experimental values.

At the same time, the use of $\Delta E'$ may lead to errors due to the difference in the correlation energies of the ion formed and the initial molecule. This often results in lower values of the ionisation potentials I compared to the experimental ones. The results obtained according to Koopmans theorem may be corrected (for example, by changing the calculated values of I by 8%), however, such corrections give satisfactory results only for ionisation from the two lowest MOs.

As an alternative, averaged values of ionisation potentials obtained by the two above-mentioned methods can be used for a comparison of calculated and experimental results.[23] But this artificial approach does not lead to good results in all cases.[4]

According to the Frank–Condon principle, the internuclear distance should be kept constant as an electron is detached. But there is no reason to state that the ion formed in this case will be in its ground state. It is more probable that the interatomic distances of the ground state of the initial molecule correspond to an excited vibrational state of the ion. In this case, the so-called vertical ionisation potential I_v, which can be determined, for instance, by the electron impact method, includes energy from the excitation of the molecule in addition to the adiabatic ionisation potential (I_a). Discrepancies between the values of I_v determined in different studies are sometimes equal to 0.15–0.40 eV.[4, 64] At the same time, the accuracy of the experimental determination of the adiabatic ionisation potentials is very high ($\pm$ 0.01–0.02 eV).[4]

Adiabatic ionisation potentials, which correspond to the difference in the energy of ground states of the ion and molecule, can be measured with high precision using spectral and photoionisation methods.

Obviously, calculation of the adiabatic ionisation potentials requires that the difference in energies of the ion and molecule, calculated for optimised geometries corresponding to the energy minima of both particles, should be determined. Ionisation potentials calculated according to Koopmans theorem should correspond to the experimentally determined vertical ionisation potential. However, the change in, for example, energies of HOMOs calculated by the Hückel method as well as by EHT, CNDO, INDO methods [12, 69–74] for a series of haloethylenes corresponds to a change in the first adiabatic potentials and at the same time does not reflect changes in the vertical potentials. Therefore, in many studies the first ionisation potentials I_a of haloethylenes calculated using the corresponding parametrisation are taken to be equal to the energy of the HOMO.

Surprisingly, the best results were obtained using the Hückel method. Presumably, it is a relatively simple procedure to adjust the parameters required for the calculations using experimental data for a small subset of molecules that accounts for this fact.

Of course, it is possible to try to adjust the corresponding parameters for calculations of ionisation potentials of haloethylenes within semiempirical SCF quantum-chemical methods. However, such a procedure and subsequent calculations are much more time-consuming than the corresponding calculations by the Hückel method. Thus, merely from a pragmatic viewpoint, the results [71–73] are still timely, and a similar approach can be successfully applied for other classes of compounds.

Attempts at calculations of ionisation potentials of fluoroethylenes using various semiempirical and non-empirical versions of the SCF method did not, in general, lead to positive results. The most complete study of ionisation potentials of molecules of the

Table 2. Calculated and experimental values of the first adiabatic ionisation potentials of haloethylenes (eV).

Molecule	Calculation [79] (see [a])	Calculation [72, 73]	Experiment [67, 68, 80]	Experiment [67, 81]	Experiment [26, 82–85]
$FHC=CH_2$	–	10.40	10.37	10.36±0.015	10.37±0.02
$F_2C=CH_2$	–	10.32	10.31	10.29±0.01	10.31±0.02 10.30±0.02
cis-FHC=CHF	–	10.30	–	10.23±0.02	10.25±0.02
trans-FHC=CHF	–	10.30	–	10.21±0.02	10.19±0.02
$F_2C=CHF$	–	10.21	–	10.14±0.02	10.14±0.02
$F_2C=CF_2$	–	10.12	10.11	10.14	10.12±0.02
$ClHC=CH_2$	10.06	10.00	10.00±0.02	9.995±0.01	10.00±0.02
cis-ClHC=CHCl	–	9.64	9.65±0.01	9.63±0.01	9.66±0.02
trans-ClHC=CHCl	9.65	9.64	9.64±0.02	9.65±0.01	9.64±0.02
$Cl_2C=CH_2$	9.89	9.89	9.83	9.79±0.02	–
$Cl_2C=CHCl$	9.49	9.50	9.48±0.03	9.47±0.01	–
$Cl_2C=CCl_2$	–	9.32	9.34±0.03	9.32±0.02	–
$BrHC=CH_2$	9.93	9.89	–	9.80±0.02	9.82±0.02
cis-BrHC=CHBr	–	9.45	–	9.45±0.02	9.45±0.02
trans-BrHC=CHBr	9.46	9.45	–	9.47±0.02	9.46±0.01
$Br_2C=CHBr$	9.22	9.30	–	9.27±0.02	–
cis-FHC=CHCl	9.92	9.91	–	–	9.86±0.01; 9.87±0.01
trans-FHC=CHCl	9.89	9.91	–	–	9.87±0.02
cis-FHC=CClF	9.93	9.89	–	–	9.86±0.02
trans-FHC=CClF	9.90	9.89	–	–	9.83±0.02
$F_2C=CHCl$	–	9.84	9.84[b]	–	–
$F_2C=CCl_2$	–	9.70	9.65	–	9.69±0.01
$F_2C=CClF$	–	9.81	9.84	–	9.82 9.76
$FClC=CH_2$	–	9.98	9.97[b]	–	–
$F_2C=CBrF$	–	9.71	9.67[b]	–	–

[a] In Ref. 79, the results of calculations on fluoroalkenes by the Hückel method with different complicating corrections were also given. [b] Experimental data were obtained after publication of the corresponding results of calculations.[72, 73]

class considered was performed by the *ab initio* MO LCAO method in the DZ basis set,[23] these values were calculated both according to Koopmans theorem and as a difference in total energies of the ion formed and the initial neutral molecule. However, even the direction of change of the calculated ionisation potentials did not correspond to the change in experimental adiabatic and vertical ionisation potentials (see Refs 4, 23, 64 and results of Refs 32, 75–78). Possible reasons for this fact have already been mentioned.

Table 2 shows adiabatic ionisation potentials of haloethylenes calculated by the Hückel method. Differences between the calculated and experimental values do not exceed a few hundredths of an electron-volt. This suggests that the calculated ionisation potentials of 28 haloethylenes (Table 3) for which there are no experimental data are also reliable. After publication of the studies [72–74], adiabatic ionisation potentials of some mixed haloethylenes were measured; for them, good agreement between the calculated and experimental data was also observed (Table 2).

Table 2 shows that experimental ionisation potentials of *cis*- and *trans*-1,2-haloethylenes are virtually identical, and this fact justifies the application of the computational methods that do not take into consideration geometrical differences between the isomers.

It should be noted that according to mass spectrometric data,[84, 86] the first ionisation potential of fluoroethylenes can be interpreted as the energy of a π-electron of the C=C bond (taken with the opposite sign). This conclusion can also be derived from the calculations on these molecules by the CNDO, INDO, MNDO, and *ab initio* methods (see Refs 4 and 64): the orbital formed by a π-bonding orbital of ethylene perturbed by fluorine atoms has the highest energy of all the π-orbitals.

The great scatter of experimental data on electron affinity (A) does not allow one to derive unambiguous conclusions on changes in A for fluoroethylenes. For example, in a reference book,[83] the value $A > -2.15$ eV is indicated for ethylene, while for fluoroethylenes the data are absent. In more recent studies,[54, 87] the values of A for C_2H_4 and $CH_2=CHF$ are -1.74 eV and -1.91 eV, respectively, *i.e.* ethylene manifests a higher electron affinity than monofluoroethylene. However, a non-empirical calculation [54] (MP2, 6-31G**/HF/6-31G* basis) gives other results: -1.86 eV and -1.62 eV. The same result was obtained in Ref. 88: calculations by the CNDO and X_α methods as well as non-empirical calculations using the Hartree–Fock functions in 6-31G and 6-31G* basis sets lead to a more stable lowest vacant orbital in fluoroethylenes compared to that in ethylene. Only the inclusion of *d*-functions into the 6-31G* basis set gives agreement with the above experimental results.

Table 3. Calculated [73] first adiabatic ionisation potentials (I_a/eV) for haloethylenes (experimental data for the given molecules are absent).

Molecule	I_a	Molecule	I_a
$Br_2C=CH_2$	9.81	ClBrC=CHBr	9.34
$Br_2C=CBr_2$	9.09	FBrC=CHBr	9.42
FBrC=CH_2	9.88	$Cl_2C=CClF$	9.45
ClBrC=CH_2	9.84	$Cl_2C=CClBr$	9.26
FHC=CHBr	9.80	$Br_2C=CBrF$	9.26
ClHC=CHBr	9.54	$Br_2C=CClBr$	9.15
ClBrC=CHF	9.74	$F_2C=CBr_2$	9.61
FBrC=CHCl	9.52	$Cl_2C=CBr_2$	9.21
FClC=CHBr	9.50	FClC=CClF	9.57
$F_2C=CHBr$	9.73	FBrC=CBrF	9.39
$Cl_2C=CHF$	9.79	ClBrC=CBrCl	9.20
$Cl_2C=CHBr$	9.39	$F_2C=CClBr$	9.64
$Br_2C=CHF$	9.70	$Cl_2C=CBrF$	9.36
$Br_2C=CHCl$	9.41	$Br_2C=CClF$	9.36
FBrC=CHF	9.79	FClC=CBrF	9.48
FClC=CHCl	9.61	FClC=CClBr	9.40
ClBrC=CHCl	9.45	FBrC=CClBr	9.30

Probable experimental errors have also to be taken into account. However, due to the lack of experimental data, this question is open to discussion.

2. Dipole moments of molecules

The polarity of a molecule can substantially affect its reactivity and reaction mechanisms. Problems arising in quantum-chemical calculations of dipole moments have been considered in a number

Table 4. Calculated and experimental values of dipole moments of fluoroalkenes.

Molecule	Method of calculation [a]	Dipole moment /D	
		calculation	experiment
FHC=CH_2	PPP [89]	0.77	1.427 [98]
	MNDO [90]	1.70	
	CNDO [91]	1.51	
	CNDO [12]	1.585	
	CNDO [92]	1.587	
	INDO [12]	1.649	
	INDO [92]	1.686	
	INDO [93]	1.483	
	HAM/3 [94]	2.64	
	ab initio [STO-3G] [95]	0.71	
	ab initio [STO-4G] [95]	0.79	
	ab initio [STO-3G] [96]	0.90	
	ab initio [4-31G] [96]	2.10	
	MM [97]	1.43	
$F_2C=CH_2$	CNDO [99]	0.88	1.37 [101–103]
	CNDO [12]	1.389	
	INDO [93]	1.420	
	INDO [12]	1.493	
	MNDO [90]	2.03	
	HAM/3 [94]	2.69	
	ab initio [b] (see [100])		
	STO-3G.7.3	1.71 (1.83)	
	7.3.1	1.22	
	9.5	2.31	
	9.5	2.25	
	MM [97]	1.39	
cis-FHC=CHF	CNDO [99]	2.74	2.42 [102, 103]
	CNDO [12]	2.806	
	INDO [12]	2.900	
	INDO [93]	2.523	
	ab initio [b] (see [100])		
	STO-3G.7.3	3.10 (3.36)	
	7.3.1	2.62	
	9.5	3.47	
	9.5	3.55	
	ab initio [b] (RHF) [104]		
	4.31G; 6.31G	3.50 (3.60)	
	6.311G	3.53	
	6.31G*	2.81	
	6.311G*	2.91	
	MM [97]	2.42	
$F_2C=CHF$	CNDO [12]	1.459	1.30–1.32 [98]
	INDO [12]	1.534	
	MNDO [90]	1.82	
	HAM/3 [94]	2.83	
	MM [97]	1.32	
$F_2C=CClF$	CNDO [21]	0.33	0.38 [98]

[a] MM is the molecular mechanics method. [b] Results of calculations with different basis sets for experimental (gas phase),[100] standard [104], and optimised (in parentheses) molecular geometry; fixed standard parameters are as follows:[104] bond lengths C–C, C–F, and C–H are equal to 1.34, 1.33, and 1.08 Å, respectively, all angles are equal to 120°.

of studies.[4, 56] The calculated and experimental values of dipole moments of fluoroethylenes are summarised in Table 4. In the study,[94] which appeared at the same time as the monograph [4], the HAM/3 method was used for the calculation of dipole moments of 97 molecules including fluoro-, 1,1-difluoro-, and trifluoro-ethylenes. However, as indicated by the authors of Ref. 94, this method overestimates the results compared to experiment.

In most cases, the CNDO method gives the dipole moments that are in better agreement with the experimental data than those obtained by the INDO, MNDO, HAM/3, and *ab initio* methods (see Table 4).

This holds for calculations of dipole moments of other fluorine-containing molecules, such as phosphorus fluorides [4, 24, 105] and nitrogen fluorides.[4, 106] However, it should be noted that calculations by molecular mechanics are more reliable than quantum-chemical calculations.

V. Conclusion

Quantum-chemical calculations on fluoroalkenes even within the isolated molecule approximation allow one to explain or predict many subtle features of their reactions. A more complete description can be achieved by determination of the structure and stability of possible intermediates [5] (carbanions, radicals, *etc.*) and by calculation of potential energy surfaces of the reactions.

In calculations of physicochemical parameters of fluoroalkenes, semiempirical and non-empirical methods that make use of experimental molecular geometry lead to better results despite the rapid development of techniques of non-empirical calculations and determination of molecular geometry by a procedure of energy minimisation. Presumably, this is due to the fact that the geometrical parameters of fluoroalkenes (especially of non-symmetrical ones) first of all, bond angles calculated in such a way deviate strongly from the experimental values. Probably, an extension of the basis sets will finally allow one to overcome this problem.

Let us indicate some other problems that are still subjects of discussion, primarily the strength of the π-bonds in ethylene and fluoroethylenes. Our opinion on this point was outlined in the second section of this review.

Another unsolved problem was not considered here but it was extensively discussed in the monograph:[4] the relative stability of geometrical non-halogenated isomers (in particular, 1,2-alkyl-substituted ones) and 1,2-dihaloethylenes. It was established experimentally that in the first case, the *trans*-isomer is more stable than the *cis*-isomer, whilst in the second case the situation is opposite. However, discussions on the probable reasons for the phenomenon still continue. We hope that all the problems mentioned will be successfully resolved in the near future.

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