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Quantum-Chemical Study of the Benzene Reaction with Fluorine

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Abstract: The reaction of benzene with fluorine atoms may be of interest as a source of phenyl and *ipso*-fluorocyclohexadienyl radicals or as a method for fluorobenzene gas phase synthesis. The structures and electronic energies of the equilibrium configurations and transition complexes of the C_6H_6F system are calculated in the density functional approximation. It was found that the interaction of benzene with atomic fluorine can proceed via two channels: hydrogen abstraction with the phenyl radical formation, and hydrogen substitution with the *ipso*-fluorocyclohexadienyl radical as primary product. Then the dissociation of the *ipso*-fluorocyclohexadienyl radical leads to creation of fluorobenzene and atomic hydrogen. The initiation of this reaction requires the activation energy near 27 kcal/mol, which indicates the low probability of this process, occurring at temperatures close to the standard (298 K). The calculations of the fluorocyclohexadienyl isomers and their cations also indicate that the formation of fluorobenzene as a product of secondary reactions is unlikely. The conclusions are confirmed by experimental data.

Keywords: gas-phase reaction; reaction mechanism; reaction path Hamiltonian; benzene; atomic fluorine; density functional theory

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1. Introduction

Chemical reactions between benzene and fluorine atoms began to attract the close attention of investigators more than fifty years ago [1]. Initially, the interest was due to the possibility of using hydrogen abstraction in studies of the structure and properties of free radicals as a source of phenyl and fluorocyclohexadienyl radicals [1,2]. Later, it was found that the interaction of benzene with fluorine atoms also results in the formation of fluorine-substituted derivatives of benzene in high yield, which made it possible to consider this reaction as a method for their synthesis [2,3].

Analysis of the electron paramagnetic resonance (EPR) spectra showed that the mixture of benzene and molecular fluorine during photolysis in an argon matrix presumably contains fluorocyclohexadienyl and phenyl radicals [1]. Based on this observation, a mechanism for benzene fluorination was proposed, which includes the reactions of hydrogen atom detachment followed by fluorine attachment:

$$C_6H_6 + F \rightarrow C_6H_5 + HF, \quad (1)$$

$$C_6H_6 + F \rightarrow C_6H_6F. \quad (2)$$

The formation of the fluorocyclohexadienyl radical has been confirmed later in molecular crossed beams experiments [4–9] and argon matrix [10].

At pressures of 0.4–4.0 atmosphere, the only stable product of gas-phase benzene fluorination is fluorobenzene. The reaction yield weakly depends on the pressure in the reaction vessel and varies in the range of 6–10% [11]. In order to explain this result, reaction (2) has been supplemented by stages of vibrationally excited fluorocyclohexadienyl radical $C_6H_6F^*$ formation, followed by collisional relaxation and dissociation, i.e.,

$$C_6H_6 + F \rightarrow C_6H_6F^* \rightarrow C_6H_6F \rightarrow C_6H_5F + H. \quad (3)$$

The presence of fluorobenzene in benzene fluorination products has been also confirmed by reactions in crossed molecular beams [7,8,12,13] and in a low-pressure flow reactor [2]. Experimental measurement of the ratio between rate constants of reactions (1) and (3) revealed that substitution (3) is the main channel of benzene fluorination [2,13,14]. In particular, the yield of fluorobenzene in the low-pressure flow reactor was estimated at $80 \pm 20\%$ [2], which significantly differs from another assessment [11].

The aim of this study is the calculation of structures and electronic energies of both equilibrium configurations and transition state complexes of the system $C_6H_6 + F$, which will make it possible to formulate a conclusion about the reaction mechanisms of hydrogen abstraction and substitution in benzene. The only known theoretical work related to this topic is devoted to complexes of benzene with halogens, including isomers of the fluorocyclohexadienyl radical [15]. The next sections of the article contain a thorough description of the calculation method, the main results, and a summary discussion.

2. Calculation Method

In order to isolate the reaction channels, we used the reaction path Hamiltonian approach. Taking into account the number of electrons in the system C_6H_6F, the density functional method (DFT) has been used to calculate the potential energy surface (PES) of the ground electronic state in the stationary points. The type of the functional, as far as the basis set of atomic orbitals (AO) has been calibrated during the calculations in order to reach sufficient agreement with reference data. It was shown previously that hybrid *meta*-functionals of the M06–M08 families make it possible to estimate the thermodynamic effects in the reactions of organic compounds with good accuracy [16–18], so as candidates we used M06, M06-2X, and M08-HX functionals. In the calculations we used basis sets A: 6-31++G** [19–21], B: aug-cc-pVDZ [22,23], and C: cc-pVTZ [22]. Diatomic molecules HF and CF were used as model systems for comparing functionals and AO bases. All calculations have been performed by the ab initio program package GAMESS US [24,25].

Comparison of the obtained results revealed that for HF and CF molecules the best agreement with the experimental data [26–28] for R_e (equilibrium internuclear distance), w_e (vibrational constant), and D_e (dissociation energy) observed in basis C (functional M08-HX). Deviation for R_e is not more than 0.002 Å, for w_e is about 10 cm^{-1}, and for D_e is less than 0.15 eV (3.5 kcal/mol). In other combinations of the basis and functional, it is not possible to achieve simultaneous reproduction of the target parameters both for HF and CF (see Table 1). Subsequently, the functional M08-HX (basis C) has been chosen as a method for the further search of the PES stationary points.

To check the accuracy of the chosen method, we have performed energy calculations of transition state complexes and equilibrium configurations of the reaction participants, i.e.,

$$CH_4 + F \rightarrow CH_4F \rightarrow CH_3 + HF. \quad (4)$$

This reaction has been selected due to the fact that the rate constants of hydrogen abstraction reactions (1) and (4) have similar values [29,30].

Table 1. The values of parameters R_e (Å), w_e (cm^{-1}), and D_e (eV) for HF and CF molecules.

Method	AO Basis	HF ($X^1\Sigma^+$)			CF($X^2\Pi$)		
		R_e	w_e	D_e	R_e	w_e	D_e
B3LYP	A	0.9277	4075	5.96	1.2901	1270	5.65
	B	0.9259	4066	5.97	1.2906	1244	5.62
	C	0.9225	4094	5.94	1.2761	1305	5.80
M06	A	0.9196	4225	6.11	1.2786	1331	5.73
	B	0.9182	4238	6.09	1.2785	1305	5.67
	C	0.9153	4230	6.04	1.2622	1371	5.91
M06-2X	A	0.9227	4180	5.93	1.2781	1337	5.67
	B	0.9212	4167	5.94	1.2788	1311	5.66
	C	0.9183	4193	5.94	1.2681	1358	5.78
M06-HX	A	0.9234	4128	6.10	1.2842	1294	5.65
	B	0.9213	4113	6.10	1.2848	1261	5.64
	C	0.9183	4135	6.05	1.2726	1316	5.73
CCSD(T)	A	0.9250	4123	5.77	1.3012	1253	5.26
	B	0.9239	4080	5.84	1.3056	1206	5.20
	C	0.9163	4193	5.97	1.2735	1332	5.61
Experiment	–	0.9168 [a,b]	4138 [a]	6.14 [b] 6.11 [c]	1.2718 [a]	1308 [a,d]	5.50 [e] 5.75 [f]

[a] Ref. [26]; [b] Ref. [27]; [c] Ref. [31]; [d] Ref. [28]; [e] Ref. [32]; [f] Ref. [33].

For reaction (4) the relative energy of reaction products is E(4) = E(CH_3 + HF) = −29.6 kcal/mol. The zero here is the energy of the initial reactants with zero point energy (ZPE) correction. Theoretical estimation of the enthalpy of reaction under standard conditions (here and below we use values p = 101,325 Pa and the temperature T = 298.15 K for pressure and temperature) is $\Delta H^0_R(4)$ = −28.9 kcal/mol, that is 2.6 kcal/mol more than the experimental values [34,35]. The experimental value of the activation energy is estimated in the range of 0.4–1.9 kcal/mol [36,37], and the best theoretical result is about −0.1 kcal/mol whereas other estimations lie in the range from −2.66 to 1.70 kcal/mol [38]. The calculated value of relative energy of the transition complex is E(CH_4F) = −1.5 kcal/mol, which is in good agreement with the theoretical estimations given in [38].

The reaction (4) and its analogs have two channels, i.e., CH_4 + F($^2P_{3/2}$) and CH_4 + F($^2P_{1/2}$), differing in energy by 400 cm^{-1} (1.14 kcal/mol), with various transition complexes and the states of the products. To date, the employed experimental methods do not imply separate measurements of the rate constants of reaction (4) for the $^2P_{3/2}$ and $^2P_{1/2}$ components of the ground state of the fluorine atom [34,38]. As a consequence, both components must be present in the reaction mixture in a ratio depending on the method of atomic fluorine obtaining. Since the experimental activation energy of the reaction (4) (0.4–1.9 kcal/mol [36,37]) is close to the energy difference between the components of the fluorine electronic ground state, the corresponding rate constant measuring results are impossible to explain without dividing into $^2P_{3/2}$ and $^2P_{1/2}$ components of the fluorine atom ground state. Nevertheless, the close values of the experimental and theoretical values of the rate constants [34,38] indicate the possibility of using nonrelativistic semi-empirical PESs to interpret the experiments.

The theoretical estimates of the reaction enthalpy ΔH^0_R (4) under standard conditions (hereinafter, pressure is p = 101,325 Pa, and temperature is T = 298.15 K) are −28.9 kcal/mol (cc-pVTZ basis)), −29.9 kcal/mol (cc-pVQZ), −30.6 kcal/mol (aug-cc-pVTZ) and −30.8 kcal/mol (aug-cc-pVQZ) and converge to experimental values of −31.3 . . . −31.5 kcal/mol [34,35]. On the contrary, the relative energies (zero is taken to be the energy of the initial reactants with corrections for the energies of the main vibrational states) of the transition complex for the same AO basis range from −1.5 kcal/mol up to −1.0 kcal/mol, differing significantly from the experimental values of the activation energy [36,37].

The discrepancy between the experimental and theoretical values of the reaction (4) activation energies is not the result of the AO basis incompleteness or an unbalanced description of the CH_4F transition complex and its dissociation products. However, it can be considered a method error when interpreting the results of nonrelativistic calculations.

3. Results and Discussion

On the base of the selected version of density functional (M08-HX, basis C), the equilibrium geometry configurations of *ipso*-, *ortho*-, *meta*-, *para*-fluorocyclohexadienyl radicals (C_6H_6F), van der Waals complex ($C_6H_5F{\cdot}H$), and transition state complexes corresponding to the reactions (1) and (2) have been found (Table 2). Structures of equilibrium configurations and transition state complexes of fluorocyclohexadienyl radicals are presented in Figure 1. The obtained internuclear distances and bond angles for *ipso*-fluorocyclohexadienyl radical agree with the values calculated by B3LYP and BH&HLYP [15].

To identify the reaction channels with the found transition states, the minimum energy pathways were calculated for all transition states. Based on the analysis of stationary points and reaction pathways of the ground electronic state PES of C_6H_6F the next reactions can be expected (see Figure 2).

$$C_6H_6 + F \rightarrow TS_1 \rightarrow C_6H_5 + HF, \quad (5)$$

$$C_6H_6 + F \rightarrow C_6H_6F \rightarrow TS_2 \rightarrow C_6H_5F{\cdot}H \rightarrow C_6H_5F + H. \quad (6)$$

Table 2. The main properties of stable participants and transitional complexes of hydrogen abstraction and substitution reactions. The values of the electron energies E_{el} and the ground vibrational state energies E_{ZPE} are given in Hartree units. The rotational constants A, B, C are given in cm^{-1}.

Intermediates	Symmetry	E_{el}	E_{ZPE}	Rotational Constants		
				A	B	C
C_6H_6(benzene)	D_{6h}	−232.272728	0.100943	0.191627	0.191568	0.095799
ipso-C_6H_6F	C_s	−332.052150	0.102067	0.164504	0.086938	0.061077
ortho-C_6H_6F	C_s	−332.057841	0.101582	0.176125	0.083502	0.057234
meta-C_6H_6F	C_s	−332.055540	0.101194	0.176568	0.082452	0.056778
para-C_6H_6F	C_s	−332.054249	0.101224	0.178196	0.081805	0.056636
$C_6H_5F{\cdot}H$	C_s	−332.016714	0.094209	0.175458	0.082774	0.059285
C_6H_5(phenyl)	C_{2v}	−231.580403	0.087849	0.211608	0.188592	0.099719
C_6H_5F	C_{2v}	−331.512398	0.092807	0.190805	0.086191	0.059372
TS_1	C_s	−331.999392	0.097821	0.178590	0.061472	0.047088
TS_2	C_s	−332.002118	0.094882	0.181664	0.084046	0.058891
HF	$C_{\infty v}$	−100.447456	0.009419	0.000000	20.869525	20.869525
F	—	−99.725232	—	—	—	—
H	—	−0.499810	—	—	—	—
ipso-$C_6H_6F^+$	C_s	−331.774657	0.102266	0.174515	0.085669	0.058663
ortho-$C_6H_6F^+$	C_s	−331.803116	0.103179	0.179398	0.084788	0.058169
F-$C_6H_6F^+$	C_s	−331.752715	0.101184	0.183284	0.078364	0.055143
$C_6H_5^+$	C_{2v}	−231.274621	0.085622	0.229556	0.181645	0.101405
TS_{12}	C_1	−331.770214	0.100731	0.180277	0.085217	5.851448
TS_{15}	C_s	−331.705236	0.097587	0.180956	0.082377	0.057044
TS_{25}	C_1	−331.705170	0.097199	0.180974	0.084688	0.058268

Experimental estimates of the activation energy (5) were not carried out, but it was found that the vibrational-rotational levels with quantum numbers v = 1 (0.42–0.60) and v = 2 (0.30–0.40) are maximally populated in the HF molecule. Based on this fact, an assumption that the activation barrier is close to the reaction threshold (energy of the initial reagents) has been made. Moreover, the method of competing reactions shows that the ratio of the rate constants of hydrogen detachment in methane and benzene is close to unity, that is, the activation energies of these reactions should also have close values [13,29]. The

theoretical value of the relative energy of the transition state E(TS_1) = −2.9 kcal/mol falls below the reaction threshold, and 4.4 kcal/mol below the sum of the energies of phenyl radical and vibrationally excited hydrogen fluoride (v = 2) (Figure 2), which indicates an error in the calculation method, like in the case of reaction (4), arising due to the using of non-relativistic approach.

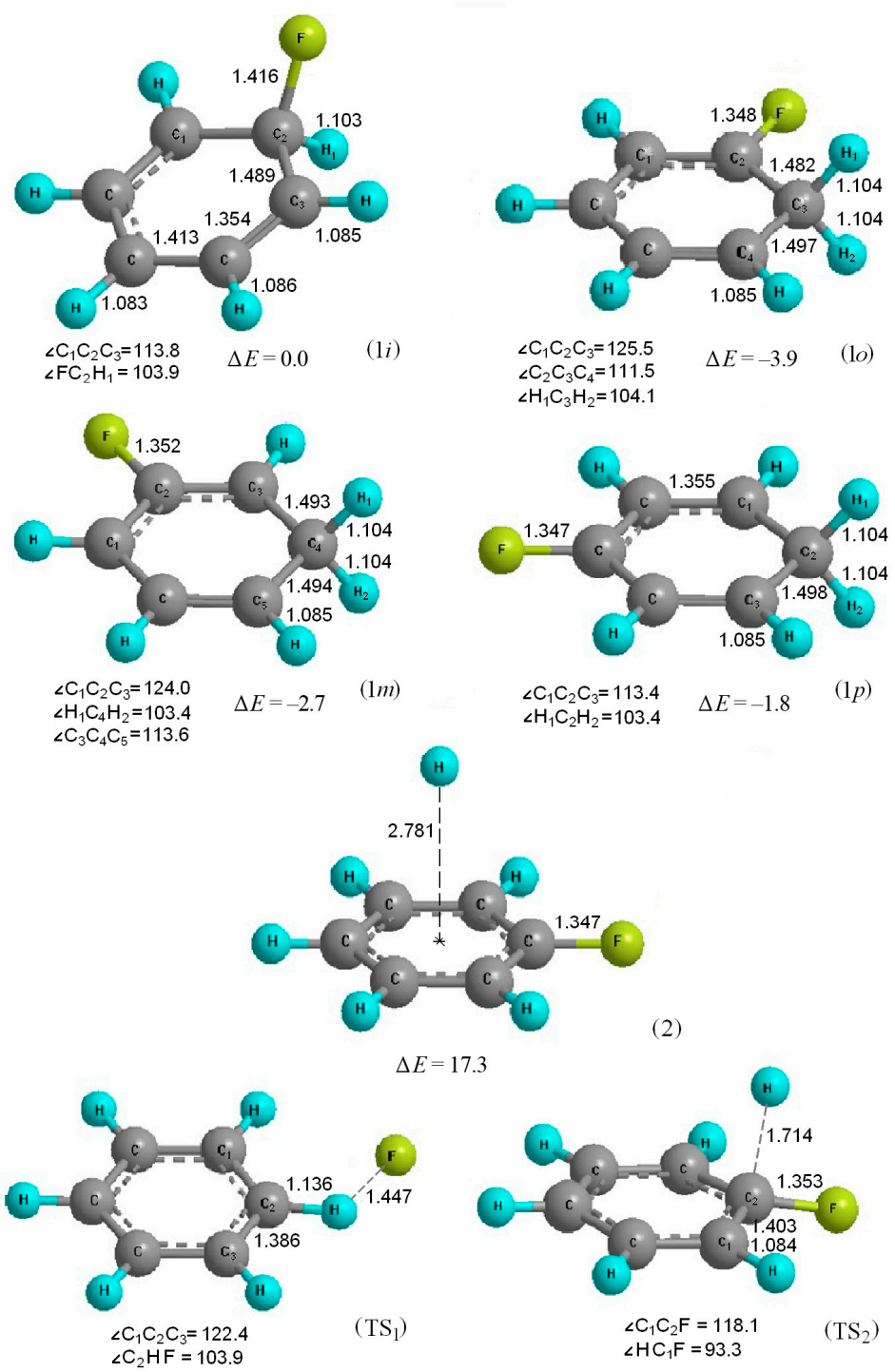

Figure 1. Structural models of (1*i*) *ipso*-, (1*o*) *ortho*-, (1*m*) *meta*-, (1*p*) *para*-fluorocyclohexadienyl radicals, (2) $C_6H_5F{\cdot}H$ complex, and transition complexes (TS_1), (TS_2). Internuclear distances and angles are given in angstroms (Å) and degrees. The relative energies (ΔE) of C_6H_6F-isomers are given in kcal/mol.

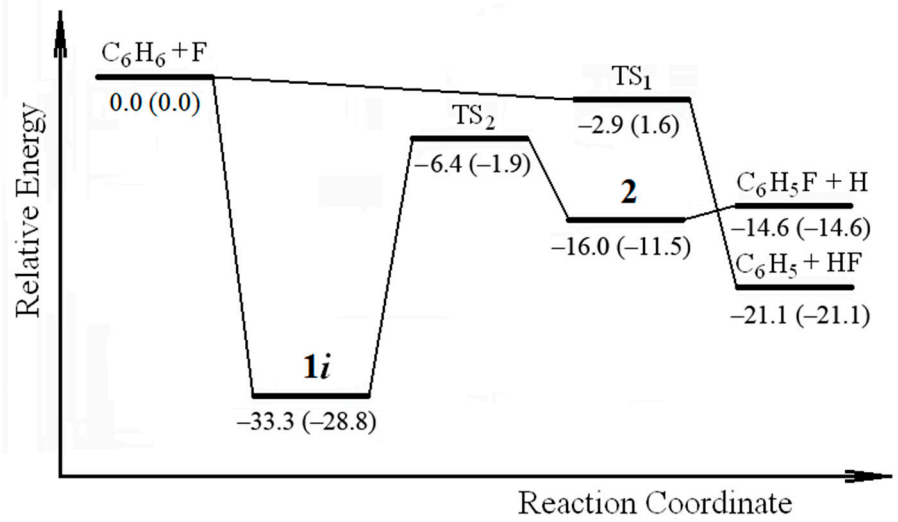

Figure 2. Reactions of detachment and substitution of hydrogen in benzene. The *ipso*-fluorocyclohexadienyl radical and complex $C_6H_5F{\cdot}H$ are denoted as 1*i* and 2 subsequently. Calculated values of the relative energies are presented without parentheses. Relative energies taking into account the error of the method are presented in parentheses. All the values of relative energies are given in kcal/mol.

The transition state for the initial stage $C_6H_6 + F \rightarrow C_6H_6F$ of the reaction (6) could not be localized. *ipso*-C_6H_6F turned out to be the closest stationary point of the PES when the initial conditions (i.e., orientation and distance between the F atom and the benzene center of mass) were varied. That is why this stage of the reaction (6) was further considered barrierless. The relative energy of the intermediate is E(*ipso*-C_6H_6F) = −33.3 kcal/mol (Figure 2). This value of the relative energy agrees well with the values calculated using the functionals BH&HLYP (−28.9 kcal/mol) and B3LYP (−34.0 kcal/mol) [15]. The substitution reaction is finalized by the dissociation of the *ipso*-fluorocyclohexadienyl radical with the formation of fluorobenzene and hydrogen atoms. This stage is an endothermic process with activation energy $\Delta E = E(TS_2) - E(ipso\text{-}C_6H_6F) = 26.9$ kcal/mol, and relative products yield $E(6) = E(C_6H_5F{+}H) = -14.6$ kcal/mol.

Comparison of experimental and theoretical values of enthalpies of reaction products (5) and (6) shows that, as in the case of the reaction (4), the PES of C_6H_6F has systematic errors (Table 3). Information about the reagents and transition state complexes of reactions (5) and (6), obtained from quantum chemical calculations, can be used to estimate the rate constants in the framework of the statistical theory of chemical reactions. In order to compensate for the error of the method, it is necessary to introduce a correction (shift) for the relative energies (enthalpies) of the initial reagents (C_6H_6 + F) and products (C_6H_5 + HF). Taking into account that the activation energy of the reaction (5) should differ little from the activation energy (4), equal to 1 kcal/mol, the correction value can be estimated as approximately −4.5 kcal/mol (Table 3).

The comparison of absorption bands in the IR spectrum [10] with the frequencies of the *ipso*-fluorocyclohexadienyl radical fundamental vibrations, calculated in the "rigid rotator—harmonic oscillator" approximation, allows us to conclude that the frequencies and intensities of the experimental and calculated oscillations in most cases are close (Figure 3). Absorption bands at 1000 and 1094 cm^{-1} differ many times in intensities, and the band at 912 cm^{-1} does not coincide with any of the calculated frequencies of fundamental vibrations. Compared with the ones of other isomers of the composition C_6H_6F (see Figure 1), coincidence with the experimental bands is not observed, which indicates about the absence of isomerization of the *ipso*-fluorocyclohexadienyl radical.

Table 3. The enthalpies of intermediates and products of benzene fluorination in kcal/mol.

Intermediate (Product)	*ipso*-C_6H_6F	ΔH^0_R (298.15 K) C_6H_5 + HF	C_6H_5F + H
Calculation	−33.9 −31.0 [a]	−20.5	−14.4
Experiment	−24.8 [b]	−25.0 [c] −25.9 [d]	−15.0 [c] −12.7 [d]

[a] Ref. [15]; [b] Ref. [9]; [c] Ref. [2]; [d] Refs. [30,39].

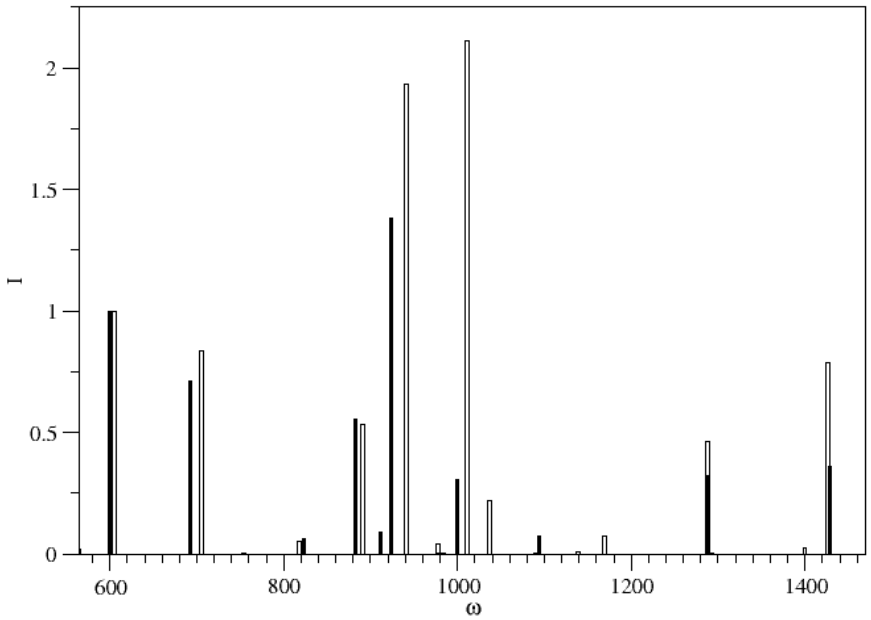

Figure 3. Absorption of the C_6H_6F radical in the IR region of the spectrum. The black bars correspond to the experimental absorption lines [10]. The empty ones correspond to the scaled values of the calculated frequencies of the *ipso*-C_6H_6F isomer fundamental oscillations with scaling factor of 0.98. Absorption intensity I is given in relative units, frequency ω is in cm^{-1}.

The calculations also do not reveal any transition complexes corresponding to the isomerization of fluorocyclohexadienyl radicals. This can be explained by the fact that the deformation of the carbon skeleton of fluorocyclohexadienyl radicals is a relatively slow process, and requires a significant amount of energy. Hence, it follows that the transition complexes corresponding to rearrangements of isomers into each other should be metastable complexes of fluorobenzene and the hydrogen atom: $C_6H_5F{\cdot}H$, with energies, close to the energy of the dissociation products of the *ipso*-fluorocyclohexadienyl radical (C_6H_5F + H), and having significant (2–3 Å) the length of one of the C-H bonds. Complexes of such structure can be formed as a result of collisions of fluorobenzene with hydrogen atoms, i.e., due to the interaction between the reaction products (6). Thus, the *ipso*-fluorocyclohexadienyl radical isomerization can be considered a negligible process.

A special consideration requires the question about the reasons for the appearance of fluorobenzene in the reaction mixture. Considering that the minimum output of 6–10% was found during the fluorination of benzene in a closed volume with radiochromatographic control of the reaction products [11], and the maximum of 80% in a low-pressure flow reactor with mass spectrometric control [2], it can be assumed that in addition to the dissociation of the *ipso*-fluorocyclohexadienyl radical (6), there may be other channels leading to its formation. The most probable can be a recombination of the fluorocyclohexadienyl radical with phenyl radical, as far as decomposition of the molecular ion $C_6H_6F^+$ directly in the chamber of the mass spectrometer.

Formally, fluorobenzene can be a product of C_6H_6F and C_6H_5 radical recombination, i.e.,

$$C_6H_5 + C_6H_6F \rightarrow C_6H_5F + C_6H_6. \quad (7)$$

This reaction is exothermic, the theoretical estimate of the reaction enthalpy is ΔH^0_R (298 K) = −94.10 kcal/mol, which indicates that the reaction is possible. The mass spectrum of benzene fluorination products contains fluorobenzene molecular ions (m/z = 96) and, in a much smaller amount, ions of phenyl radical (m/z = 77), but there are no molecular benzene ions (m/z = 78) [2]. Because there is no significant amount of benzene molecules in the mixture, the reaction (7) is unlikely.

Analysis of the experimental results shows that the molecular ion $C_6H_6F^+$ has two main dissociation channels, i.e.,

$$C_6H_6F^+ \rightarrow C_6H_5^+ + HF, \quad (8)$$

$$C_6H_6F^+ \rightarrow C_6H_4F^+ + H_2. \quad (9)$$

Channel (8) is the lowest in energy, and the channel threshold (9) is 20.3 kcal/mol lower than the threshold (8). The main stable dissociation product is HF, which corresponds to the decay through the channel (8), whereas contribution to the dissociation from (9) does not exceed 4% [40–42].

Theoretical reaction mechanism (8) predicts the possibility of rearrangement of *ortho*- and *ipso*-isomers $C_6H_6F^+$ into the ion-dipole complex $C_6H_5^+$·HF (F-isomer) followed by barrier-free dissociation into $C_6H_5^+$ and HF [40]. This result is partially confirmed by experiment: in the IR region of the absorption spectrum of the reaction mixture, there are individual lines of *ortho*- and *para*-isomers of ions $C_6H_6F^+$ [41] and ion-dipole complex $C_6H_5^+$·HF (F-isomer) [42–44]. In addition, the possibility of dissociation of *ortho*- and *ipso*-isomers $C_6H_6F^+$ was shown through metastable vibrational states, bypassing the stage of formation of F-isomer [42]. Our calculations confirm the mechanism [40], deviations in the relative energies of stable isomers and transition states do not exceed 2 kcal/mol (Figure 4). Structural parameters for the charged isomers $C_6H_6F^+$ and transition complexes are consistent with the previously calculated ones [40–43]. Summing up the intermediate result, we note that the formation of fluorobenzene as a result of the decay of isomeric ions $C_6H_6F^+$ should be assumed unlikely since the main stable products of their decay are HF and H_2.

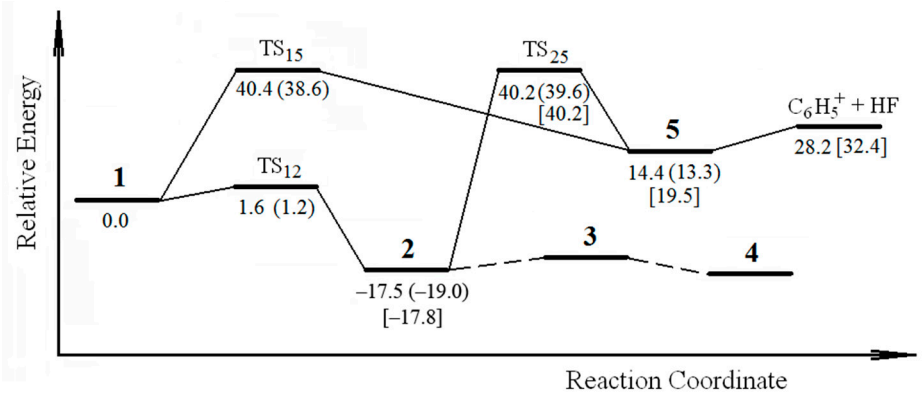

Figure 4. Isomerization and decay of the $C_6H_6F^+$ ion. The *ipso*-, *ortho*-, *meta*-, *para*-fluorocyclohexadienyl cations numbered as 1, 2, 3, and 4 correspondingly, and F–isomer $C_6H_5^+$·HF denoted as 5. Calculated values of the relative energies are presented without parentheses. The relative energies in round and square parentheses were obtained in refs. [40,41]. The relative energies are given in kcal/mol.

It remains to be assumed that fluorobenzene is formed as a result of a two-channel reaction of F and C_6H_6 (see (5), (6), and Figure 2), passing by pathway (6) through an intermediate complex $C_6H_6F^*$ (TS_2). As mentioned above, the stage of dissociation of *ipso*-

fluorocyclohexadienyl radical has a rather high activation threshold (near 26.9 kcal/mol), which indicates about low probability of this reaction occurring under standard conditions. However, in most studies, the source of fluorine atoms was the dissociation reaction $F_2 \rightarrow 2F$, activated thermally [4–9,12,13] or by high-frequency discharge [2,30,39]. The oven temperature ranged from 1023 K [4–9] up to 1100 K [12,13] whereas the fluorine thermal atomization threshold is about 650 K [12]. Temperature measurements in the reaction zone were not carried out, but in one of the works it was estimated as the arithmetic mean of the temperatures of benzene and atomic fluorine, and was rated at 660–700 K [12,13]. This estimate, despite its approximate nature, confirms the possibility of the formation of fluorobenzene in the reaction (6). Note, that the dissociation of F_2 under the influence of a microwave discharge is a typical method for fluorine atomization in the method of competing reactions [30,39,45]. In this case, the degree of F_2 dissociation was estimated at approximately 97%, which indicates a higher temperature of the reaction mixture compared to previous results [12,13].

It should be noted that the formation of fluorobenzene in the presence of methane [30] may pass through a more complex mechanism, with the formation of ions CH_5^+ and their subsequent interaction with fluorobenzene molecules, including the formation of an intermediate $CH_5^+C_6H_5F$ [44] and its dissociation in the chamber of the mass spectrometer

$$CH_5^+ + C_6H_5F \rightarrow CH_5^+C_6H_5F \rightarrow CH_4 + C_6H_6F^+. \quad (10)$$

The degree of influence of these processes on the yield of fluorobenzene has not been studied to date.

4. Conclusions

Thus, the calculations predict two channels for the interaction of benzene with atomic fluorine: the elimination of hydrogen to form the phenyl radical and the addition of fluorine to form the *ipso*-fluorocyclohexadienyl radical, in full agreement with the experimental results. Calculated values of the enthalpies of intermediates and reaction product formation are in good agreement both with their experimental values and with the values found in independent calculations. Calculations predict that dissociation of the *ipso*-fluorocyclohexadienyl radical into fluorobenzene and atomic hydrogen is unlikely at standard temperature since this stage of the reaction has a rather high activation barrier. The experimentally observed dissociation of the *ipso*-fluorocyclohexadienyl radical with the formation of fluorobenzene can be explained by the fact that the temperature of fluorine atoms (near 1000 K) is sufficient to initiate this reaction. The formation of fluorobenzene due to the occurrence of secondary reactions is unlikely.

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