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Mechanism of Electrophilic Fluorination of Aromatic Compounds with NF-Reagents*

G. I. Borodkin[a,b], P. A. Zaikin[a,b], M. M. Shakirov[a], and V. G. Shubin[a]

[a]*Vorozhtsov Novosibirsk Institute of organic Chemistry, Siberian Division, Russian Academy of Sciences, Novosibirsk, 630090 Russia*
e-mail: gibor@nioch.nsc.ru
[b]*Novosibirsk State University, Novosibirsk, Russia*

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Abstract—Kinetic isotope effects H/D in electrophilic fluorination of aromatic compounds with NF-reagents were investigated. The small values of k_H/k_D (0.86–1.00) are in agreement with the polar reaction mechanism where the Wheland complex decomposition is not the limiting stage. The fluorination of 1,3,5-trideuterobenzene was established by ^1H and ^{19}F NMR spectroscopy to occur with a 1,2-migration of a hydrogen (deuterium) atom. The analysis of Brown–Stock relationship demonstrated that the activity of NF-reagents exceeded that of many known electrophilic systems including halogenation, but it was essentially less than the activity of elemental fluorine.

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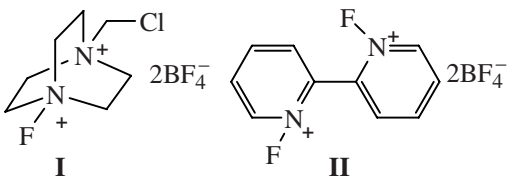
The growing interest in fluorinated aromatic compounds caused by their extensive application as drugs, pesticides, dyes, liquid crystals, and polymers requires a development of environmentally safe and economically feasible fluorination procedures [2–18]. The majority of known fluorinating reagents used for electrophilic arenes fluorination are poisonous and unsafe for handling (F_2, $FClO_3$, XeF_2, CF_3OF, AcOF etc.) [3, 4, 7, 12, 16, 19]. In the last decade extensive application in fluorination of aromatic and heteroaromatic compounds found a new class of F^+ "carriers": NF-reagents like 1-fluoro-4-chloromethyl-1,4-diazoniabicyclo[2.2.2]octane bis(tetrafluoroborates) (F–TEDA–BF_4) (**I**), 1,1-difluoro-2,2'-bipyridinium bis(tetrafluoroborates) (**II**), *N*-fluorobenzenesulfonimide (**III**) etc. [3–16].



I **II**

$(PhSO_2)_2NF$

III

Although quite a number of publications reported on properties and synthetic applications of NF-reagents the mechanism of electrophilic aromatic fluorination at their use remains free to discussion [5, 6, 9–11, 16, 19, 20]. The observed prevalence of ortho and para isomers with respect to electron-donor substituent in the benzene ring shows that the NF-reagents exhibit electrophilic properties [9, 12, 20] (cf. [19]). Inasmuch as the formation of F^+ cation is thermodynamically extremely unfavorable (its enthalpy of formation in the gas phase ΔH_f is 1760 kJ mol^{-1}) compared with Cl^+, Br^+, I^+ (ΔH_f 1370, 1260, and 1120 kJ mol^{-1} respectively) [6] the formation of the cation in the course of electrophilic aromatic fluorination is hardly expectable, and the NF-reagents are regarded as the source of "pseudopositive" or "electrophilic" fluorine [9]. Therefore generally two routes are considered for fluorine atom transfer to the arene: nucleophilic substitution at the fluorine atom (polar S_EAr mechanism) and one-electron transfer involving into the process a cation radical (SET mechanism) (Scheme 1).

NF-Reagents are either neutral (R_2NF) or salts with a positively charged cation (R_3NF^+), and these facts should be taken into account in the treatment of the mechanism of arenas electrophilic fluorination. The nature of the aromatic compound is also essential, especially its

* For preliminary communication, see [1].

capability of oxidation. In a general case various fluorination mechanisms might operate depending on the character of the NF-reagent, aromatic compound, and the reaction conditions. In [20, 21] the comparison of experimental fluorination rate constants of naphthyllithium, potassium 2-methyl-3,4-dihydro-1-naphtholate and a series of other compounds in reaction with 2-fluoro-3,3-dimethyl-2,3-dihydro-1,2-benzisothiasole 1,1-dioxide with the values calculated from the standard redox potentials E^o in keeping with Marcus theory led to the conclusion that the preferable mechanism was the polar one, S_EAr (cf. [22]). The high substrate selectivity in the fluorination of mesity-lene (MesH) and durene (Dur) with the reagent F–TEDA–BF_4 ($k_{MesH} : k_{Dur} = 6–10$) also testifies to the reaction proceeding by the polar mechanism [23]. In contrast in several studies on the fluorination of aromatic compounds and olefins arguments were advanced supporting the SET mechanism [24–31], and therewith the lifetime of the pair cation radical– fluorine atom was very short (10^{-13}–10^{-15} s) [16]. In this event according to [32] the arguments "pro" and "contra" SET mechanism become senseless [16]. Both considered mechanisms, SET and S_EAr, involve a formation of σ-complex, or Wheland complex, which through proton elimination transformes into fluorinated aromatic derivative.

The target of this study was investigation of the mechanism of electrophilic fluorination of arenes with NF-reagents applying kinetic isotope effects and the estimation of activity of the reagents as compared with other electrophiles using Brown–Stock relationship.

As fluorination objects we selected monocyclic and bicyclic arenas: benzene, toluene, mesitylene, and naphthalene. As already mentioned, the fluorination of mesitylene and durene with reagent **I** occurred presumably by the polar mechanism [23]. Whereas the ionization potential of benzene (9.24384 eV), toluene (8.8276 eV), and naphthalene (8.1442 eV) is higher than that of durene (8.025 eV) [33] the SET mechanism for these compounds is also hardly probable.

The kinetics of mesitylene reaction with fluorinating reagent **I** in MeCN fits to the polar mechanism (Scheme 2).

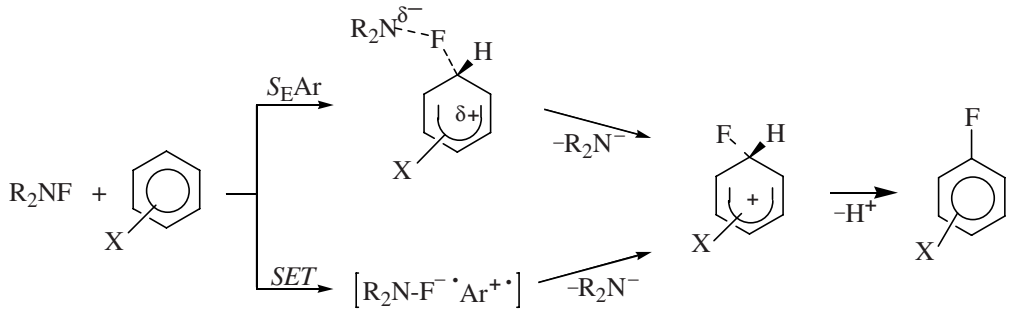
The dependence of rate constant k on time t in the approximation of a quasistationary concentration of the σ-complex is described by the following expression:

$$\ln([MesH]/[\mathbf{I}]) = k([MesH]_0 - [I]_0)t + \ln([MesH]_0/[\mathbf{I}]_0), \quad (1)$$

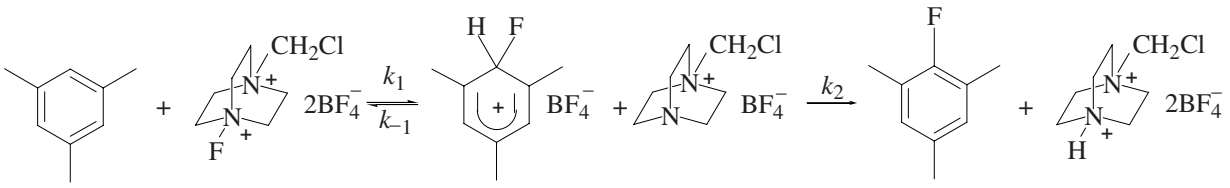
where $k = k_1k_2/(k_{-1})(k_{-1} + k_2)$.

A good linear correlation exists between the values ln([MesH]/[**I**]) and current time t with r 0.9999. From the obtained values of second order rate constants [$k_{273.2K}$ $(1.41 \pm 0.02)\times10^{-5}$, $k_{303.8K}$ $(5.67 \pm 0.04)\times10^{-4}$, $k_{312.0K}$ $(1.85 \pm 0.01)\times10^{-3}$, $k_{323.0K}$ $(5.54 \pm 0.08)\times10^{-3}$ l/(mol s)] the following activation parameters were evaluated: E_a 88 ± 3 kJ mol^{-1}, log A 12.0 ± 0.5, $\Delta H^{\neq}$ 86 ± 3 kJ mol^{-1}, $\Delta S^{\neq}$ –24 ± 9 J/mol K. The large $\Delta H^{\neq}$ and small absolute value of $\Delta S^{\neq}$ correspond to the enthalpy control of the fluorination where the C–F bond formation occurs in the rate-limiting stage.

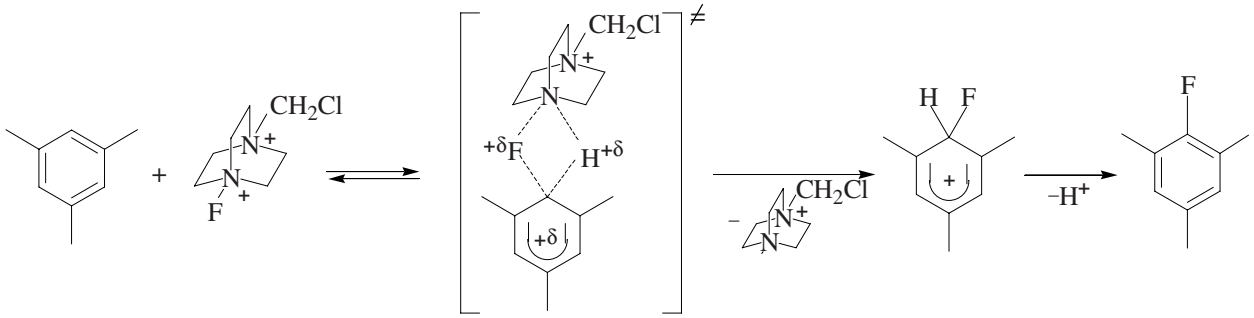
Scheme 1.



Scheme 2.



Scheme 3.



Kinetic isotope effects are extensively used for establishing the mechanisms of electrophilic aromatic substitution [34]. We estimated the values of k_H/k_D for the electrophilic fluorination of arenas with reagents **I–III** by means of GC-MS and NMR methods (Table 1). As seen from Table 1, no primary kinetic isotope effect was found ($k_H/k_D \leq 1$). This fact disagrees with the stepwise mechanism where the limiting stage is the proton abstraction from the σ-complex (Scheme 1) (cf. [34–37]). Besides the concerted mechanism with a considerable loosening of the C–H bond in the transition state is also excluded (Scheme 3).

The ratio k_H/k_D is practically unchanged at solvent variation and evidently is governed by the structural factors of substrate and the character of the fluorinating reagent. The observed variations in the secondary kinetic isotope effects in the fluorination reaction at the change of the structure of the aromatic substrate may originate from several factors superimposed. The C–H bond is more effectively involved in hyperconjugation with the partially vacant p-orbital in the arising σ-complex, and then the value $k_H/k_D > 1$, whereas the rehybridization of the carbon atom $sp^2 \rightarrow sp^3$ should provide the opposite effect ($k_H/k_D < 1$) [37]. The higher electron-donor effect of deuterium compared with protium is especially important when the deuterium is located in the positions *1*, *3*, and *5* of the σ-complex (cf. σ^+_{n-D} –0.001) [38]. The observed in the most cases $k_H/k_D < 1$ may be ascribed to the prevalence of the $sp^2 \rightarrow sp^3$ rehybridization effect and also to the large electron-donor effect of deuterium. The most active among the NF-reagents used is F–TEDA–BF_4 [39, 40]. According to Hammond rule in the event of an active agent the transition state should be early and therefore the hyperconjugation effect leading to enhanced ratio k_H/k_D should be less significant. In this connection becomes understandable some reduction in the k_H/k_D ratio at the use of the reagent F–TEDA–BF_4 as compared with the ratio for neutral reagent **III** (Table 1).

Table 1. Kinetic isotope effects in electrophilic fluorination of arenas estimated by GC-MS method

Number of NF-reagent	ArH	Solvent	Temperature, °C	k_H/k_D
I	C_6H_6/C_6D_6	MeCN	110	0.92±0.06
	C_6H_6/C_6D_6	MeCN	110	1.00±0.04[a]
	C_6H_6/C_6D_6	[bmim][BF_4][b]	110	0.89±0.02
	Mesitylene/mesitylene-1,3,5-d_3	MeCN	60	0.89±0.02
	Naphthalene/naphthalene-d_8	MeCN	60	0.86±0.01
II	C_6H_6/C_6D_6	MeCN	110	0.86±0.03
	Naphthalene/naphthalene-d_8	MeCN	60	0.91±0.05
III	Mesitylene/mesitylene-1,3,5-d_3	MeCN	110	0.99±0.03
	Naphthalene/naphthalene-d_8	MeCN	110	0.895±0.007
	Naphthalene/naphthalene-d_8	$ClCH_2CH_2Cl$	110	0.889±0.007

[a] Data reported were obtained by two measurements of ^{19}F NMR spectra.
[b] [bmim] is 1-butyl-3-methylimidazolium.

Additional proofs of σ-complexes formation in the course of electrophilic fluorination were obtained from the analysis of the products of reaction between 1,3,5-trideuterobenzene and reagent **I**. The ratio of isotopomers fluorobenzene-d_3/fluorobenzene-d_2 estimated by GC-MS method was too high (1.28). The reason of the fact is presumably the interconversion of the arising σ-complexes by 1,2-shift of a hydrogen or a deuterium atom (Scheme 4). Such 1,2-shifts in "long-lived" arenonium ions are known to occur with very high rates [41–43]. For instance, the rate constant of 1,2-shift in a benzenonium ion at 110°C calculated by Arrhenius equation [43] amounted to 4×10^9 s^{-1} and was evidently comparable with the diffusion-controlled pseudofirst order rate constant of proton elimination from the σ-complexa (~10^{10} s^{-1}) (cf. [44]).

To detect the isotopomers whose appearance may be ascribed to 1,2-shifts of hydrogen and deuterium in the formed σ-complexes we registered ^1H and ^{19}F NMR spectra of the fluorination products (Fig. 1 and 2). As expected in the ^1H NMR spectrum the resolution of similar signals of isotopomers was not observed, and the most informative was ^{19}F NMR spectrum. Analysis of the spectrum revealed the presence of isotopomers B and C whose formation was evidently due to the isomerization of σ-complexes with the rate of hydrogen (deuterium) 1,2-shift comparable to the rate of their elimination. The comparison of the calculated spectrum with the experimental one permitted the estimation of isotopomers ratio A:B:C:D (1.0:0.5:0.8:1.1). To our knowledge this is the first example of detecting rearrangement of σ-complexes involved in electrophilic fluorination of aromatic compounds.

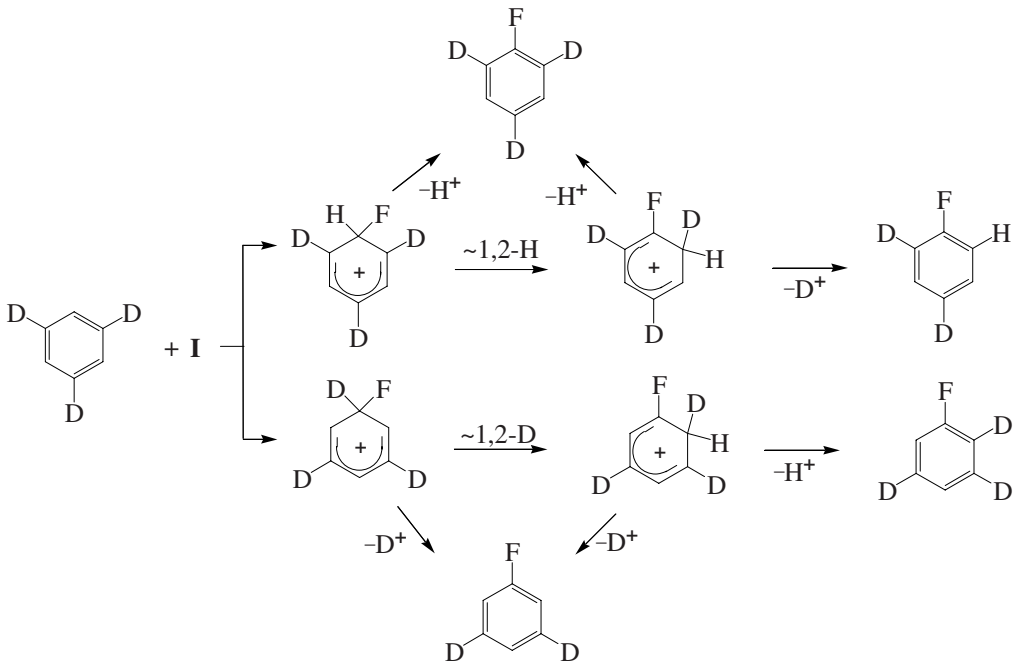
It is of interest to consider the place by activity of fluorinating reagents among the other electrophilic agents. One of the ways of this estimation is the evaluation of correlation between the substrate and position selectivity in the framework of the Brown–Stock relationship [45–47]. The comparison of substrate and position selectivity was carried out in [46] for 108 reactions of electrophilic substitution of a hydrogen atom in toluene, and the following correlation equation was obtained:

$$\log f_p = -0.17 + 1.38\, S_f,\ r\ 0.91, \qquad (2)$$

where f_p is the factor of a partial substitution rate of the hydrogen atom in the *para*-position of toluene, S_f is the selectivity factor [log (f_p/f_m)] for toluene. The correlation was improved by excluding the data on toluene nitration with the salt $NO_2^+BF_4^-$ in polar aprotic solvents and also of some other findings (8 points in total were excluded) since at the use of nitronium salts the limiting stage of the reaction was likely the formation of a π-complex [46]:

$$\log f_p = -0.08 + 1.37\, S_f,\ r\ 0.95. \qquad (3)$$

Scheme 4.



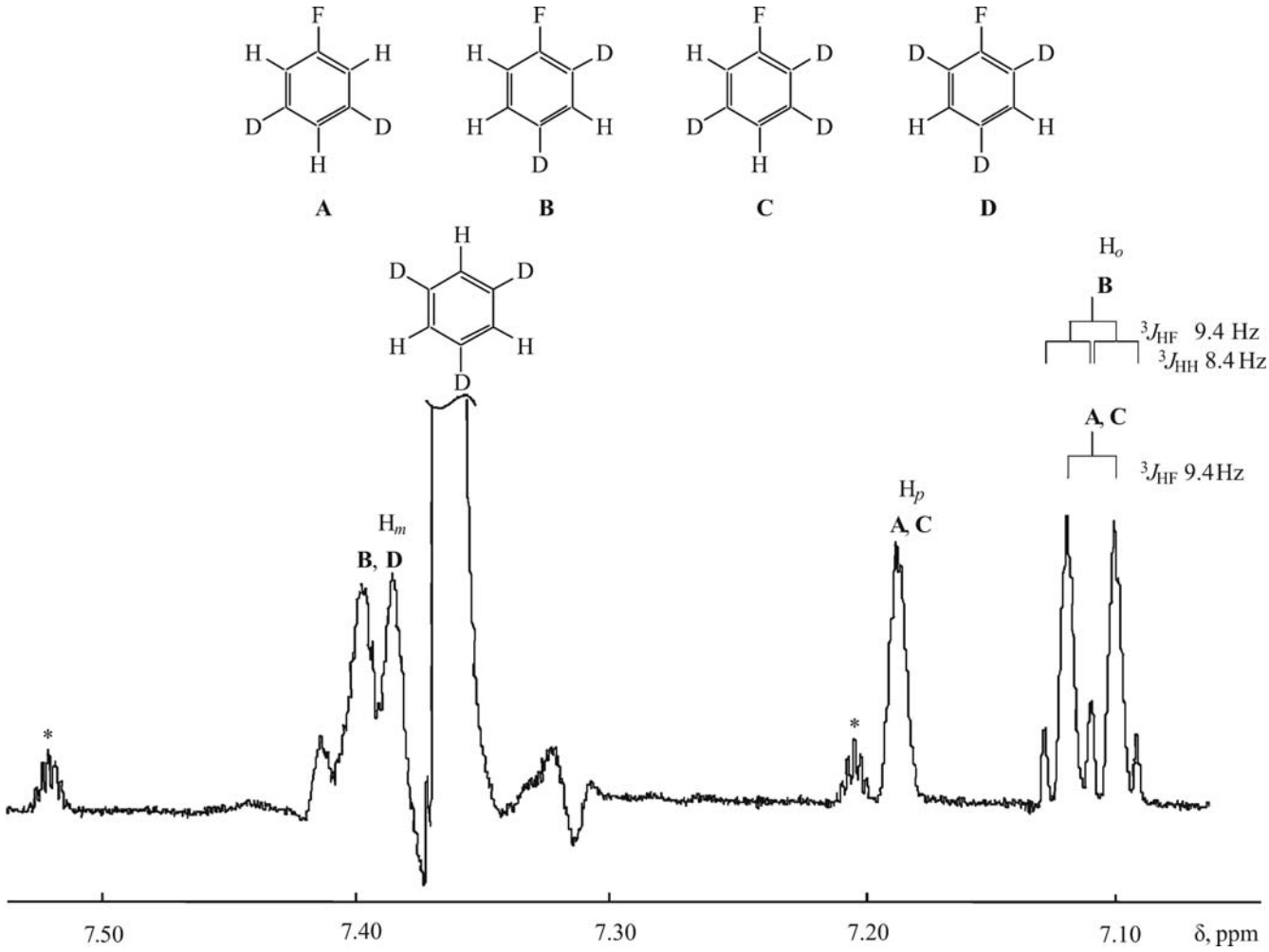


Fig. 1. ^{1}H NMR spectra of deuterofluorobenzenes (500 MHz, CD_3CN) formed in reaction of 1,3,5-trideuterobenzene with reagent **I** in CD_3CN at 110°C. Satellites due to coupling H–^{13}C and H-D in 1,3,5-trideuterobenzene are marked with asterisks.

The calculation of log f_p values by equation (3) for toluene fluorination with reagents **I–III** at 110°C gives the estimates 1.37, 1.30, and 1.18 respectively in a fair agreement with the experimental findings (Table 2). The low lgf_p and S_f values indicate that the fluorinating agents under investigation are fairly active. The comparison of $logf_p$ and S_f for the fluorination with the published data on other reactions of electrophilic aromatic substitution showed that the activity of NF-reagents exceeded that of many known electrophilic systems used for halogenation, deuteroexchange, acylation, and chloromethylation, but it was considerably lower than fluorine activity (Table 2).* The studied NF-reagents possess similar activities (cf. [49]).

A correspondance of the electrophilic fluorination with the Brown–Stock relationship indicates that the reaction fits to the laws characteristic of the most aromatic electrophilic substitutions. Presumable the stage of π-complex formation between the aromatic substrate and the fluorinating reagent is not limiting, and the structure of the transition stage is close to σ-complex.

Results of quantum-chemical calculations by PM3 method [50] for the system mesitylene–reagent **I** are consistent with the polar mechanism (Scheme 1). The calculations show that the reaction of mesitylene with the NF-reagent lead to the formation of a pair σ-complex-1-chloromethyl-4-aza-1-azoniabicyclo[2.2.2]octane E (Fig. 3) where occurs a practically complete transfer of the fluorine atom to the mesitylene molecule. The distance between N and F atoms in this pair (3.68 Å) exceeds the sum of van der Waals radii of N and F atoms (2.85 Å) [44] indicating that no significant interaction exists between the atoms. This pair formation in the gas phase

* Evidently the difference in temperatures may be neglected.

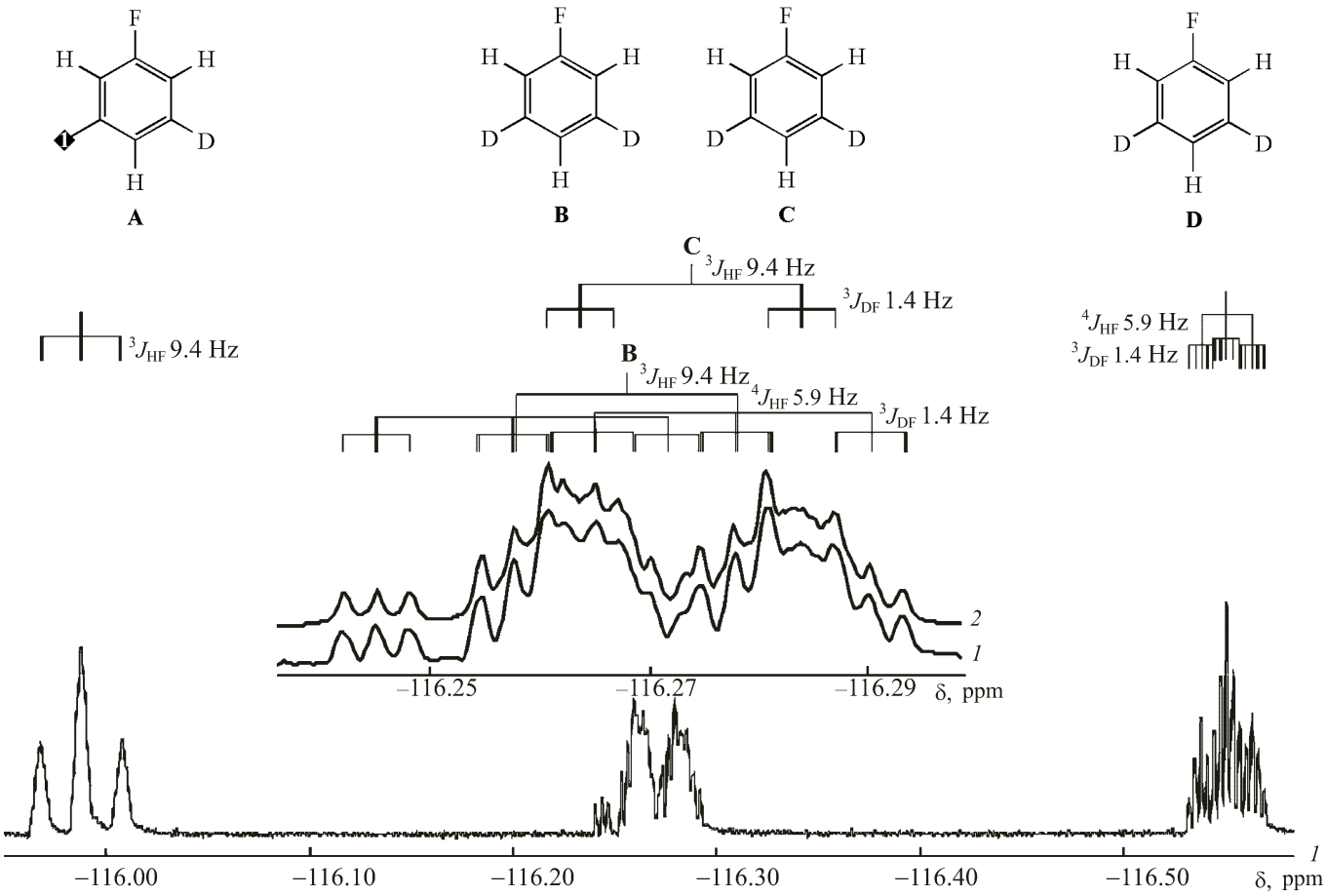


Fig. 2. ^{19}F NMR spectra of deuterofluorobenzenes (470 MHz, CD_3CN) formed in reaction of 1,3,5-trideuterobenzene with reagent **I** in CD_3CN at 110°C (1), and the calculated spectrum (2). Chemical shifts are measured from $CFCl_3$ and recalculated to the scale of the external reference C_6F_6 (–162.9 ppm).

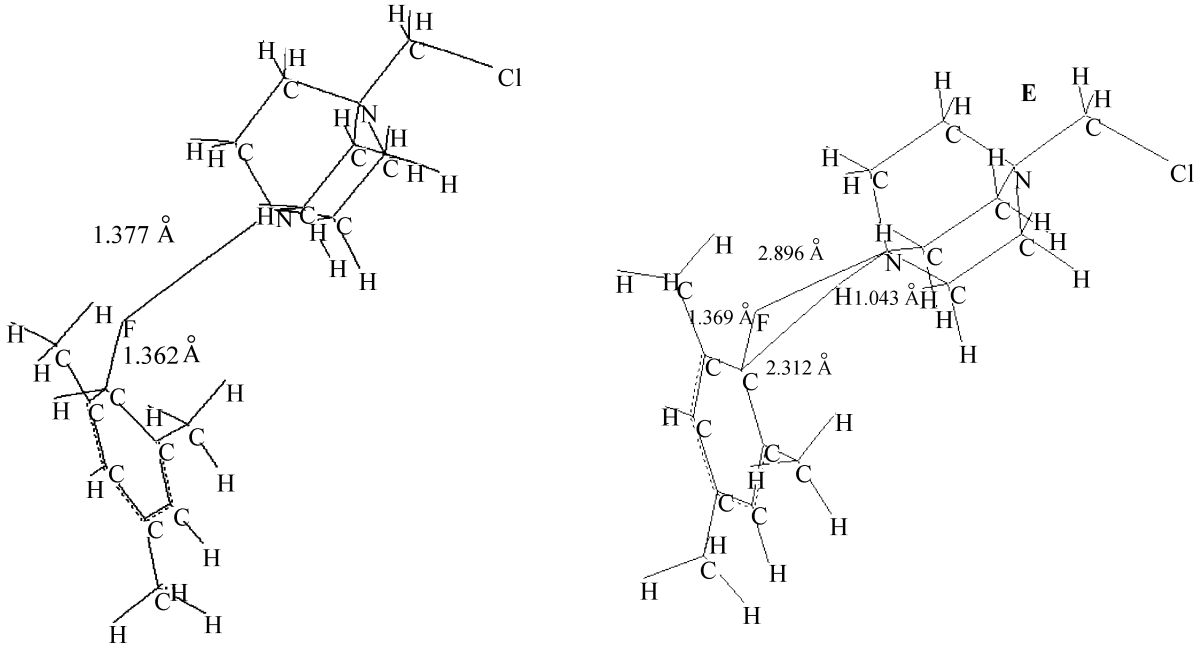


Fig. 3. Structures of mesitylene complexes with reagent **I** calculated by PM3 method.

is highly exothermal (ΔH_f –387.0 kJ mol^{-1}). On the PES of this system one more minimum is present corresponding to a structure where the hydrogen atom is transferred to the nitrogen of the fluorinating reagent (complex F) (Fig. 3), and the energy of this complex is higher by 79.0 kJ mol^{-1} than that of pair E. A significant feature of this complex is the close position of C^1 and the hydrogen of the NH fragment; therewith the distance between them is less than the value corresponding to the short contact of C and H atoms (2.52 Å) [51]. If it is considered that the transition state leading to this complex includes a four-membered fragment with a significant loosening of C^1–H bond (Scheme 3), a notable kinetic isotope effect should be observed, and consequently our experimental data rule out this alternative mechanism.

Thus the data obtained correspond to the stepwise mechanism of electrophilic fluorination of arenes by NF-reagents with the formation of σ-complex, and the stage of proton elimination from the complex is not limiting.

EXPERIMENTAL

NMR spectra were registered on spectrometers Bruker AC-200, AV-300, and DRX-500. As internal references in recording ^{1}H NMR spectra served the residual proton signals of deuterochloroform (δ 7.24 ppm) and deutero-acetonitrile (δ 1.96 ppm), and for ^{19}F NMR spectra, C_6F_6 (δ –162.9 ppm). GC-MS measurements were carried out on a Hewlett Packard G1800 instrument composed of a gas chromatograph HP5890 series **II** and mass-selective detector HP5971. Ionizing electrons energy 70 eV; oven temperature programmed as follows: 2 min at 50°C, further 10 deg/min till 280°C; vaporizer tempera-ture 280°C; ion source temperature 173°C; column 30 m × 0.25 mm, stationary phase HP-5MB (5% of diphenylsiloxane, 95% of dimethylsiloxane); carrier gas helium (1 ml/min).

Following reagents were used in the study: 1-fluoro-4-chloromethyl-1,4-diazoniabicyclo[2.2.2]octane bis-(tetrafluoroborate) purchased from Aldrich (95%), *N*-fluorobenzenesulfonimide purchased from Lancaster (95%), *N,N'*-difluoro-2,2'-bipyridinium bis(tetrafluoro-borate) purchased from Acros, KI of "chemically pure" grade, $Na_2S_2O_3$ of "pure for analysis" grade, $K_2Cr_2O_7$ of "chemically pure" grade, benzene-d_6, 1,3,5-tri-deuterobenzene, and CF_3CO_2D purchased from NPO GIPKh with deuterium content 99.6, 99.4, and 98.5 at% respectively, naphthalene-d_8 (Aldrich, 99%). Mesitylene was distilled in a vacuum and was stored over molecular sieves 4 Å. Acetonitrile was purified as in [44], stored over molecular sieves 4 Å, and was distilled over P_2O_5 under argon just before use.

Table 2.

Reagents and reaction conditions	Log f_p	S_f
Reagent **I**, ArH, MeCN, 110°C[a]	1.35	1.06
Reagent **I**, ArH, MeCN, 80°C[a]	1.38	1.16
Reagent **II**, ArH, MeCN, 110°C[a]	1.40	1.01
Reagent **III**, ArH, 110°C[a]	1.36	0.92
F_2, $C_6F_5CF_3$, 40°C[b]	0.62	0.53
Br_2, 85% AcOH, 25°C	3.384	2.644
Cl_2, AcOH, 25°C	2.914	2.219
Br_2, AcOH, 25°C	2.728	2.053
HOBr, $HClO_4$, 50% dioxane, 25°C	1.771	1.373
HOCl, $HClO_4$, H_2O, 25°C	1.914	1.311
DBr, 25°C	3.778	3.000
D_2O, CF_3CO_2H, 70°C	2.624	2.044
PhCOCl, $AlCl_3$, $PhNO_2$, 25°C	2.920	2.221
CH_3COCl, $AlCl_3$, $ClCH_2CH_2Cl$, 25°C	2.874	2.192
$PhSO_2Cl$, $AlCl_3$, 25°C	1.480	1.160
HNO_3, 90% AcOH, 45°C	1.763	1.366
$AcONO_2$, Ac_2O, 0°C	1.780	1.229
$AcONO_2$, Ac_2O, 30°C	1.709	1.226
HNO_3, CH_3NO_2, 30°C	1.664	1.297
CH_3Br, $GaBr_3$, ArH, 25°C	1.072	0.842
CH_2O, HCl, $ZnCl_2$, AcOH, 60°C	2.633	1.993
$Hg(OAc)_2$, AcOH, 25°C	1.362	1.014
$Hg(OAc)_2$, AcOH, 90°C	1.049	0.819
$Hg(OAc)_2$, $HClO_4$, AcOH, 25°C	1.517	1.165
$Hg(OAc)_2$, $HClO_4$, AcOH, 70°C	1.389	1.041

[a] Data of this study.
[b] Data from [48].

1,3,5-Trideuteromesitylene was prepared similarly to procedure [52]. Mesitylene was kept with 25-fold molar excess of CF_3CO_2D for 3 h at 60°C, excess acid was distilled off new portion of acid was added, and the procedure was repeated thrice. The residue was diluted with distilled Et_2O, washed with a saturated solution of $NaHCO_3$ and with water. The ether solution was dried with magnesium sulfate, the ether was distilled off. According to the mass spectrum the compound obtained contained 98.3 at% of deuterium.

Kinetics of mesitylene reaction with reagent I. The prepared solutions of mesitylene (0.35 mol l^{-1}) and of reagent **I** (0.07 mol l^{-1}) in acetonitrile were stored at the required temperature for 30 min, the they were mixed in such amounts that the concentration of reagent **I** was 0.05 mol l^{-1}, and mesitylene, 0.1 mol l^{-1}. The reaction

progress was monitored by the consumption of the fluorinating reagents measured in samples taken intermittently. The concentration of residual reagent **I** was evaluated iodometrically [28].

Estimation of kinetic isotope effects. The isotope effects were measured by the method of competative kinetics using GC-MS procedure (cf. [52]). The fluorinating reagent, deuterated and undeuterated substrates taken in equimolar amounts were dissolved in anhydrous MeCN (c 0.05 mol l^{-1}). After keeping the mixture at the required temperature it was diluted with a double volume of Et_2O, the salt precipitate was filtered off, and the ether was distilled off. Kinetic isotope effects were calculated by equation

$$k_H/k_D = [Ar_H]/[Ar_D],$$

where k_H, k_D are the rate constants of fluorination, $[Ar_H]$, $[Ar_D]$ are the running concentrations of undeuterated and deuterated product ArF respectively. The concentrations were evaluated from the integral intensity of the respective molecular ion peaks in the mass spectra.

Factors of partial rates of substitution in the meta and *para* positions of toluene were measured by the method of competitive kinetics. Reagents **I** or **II**, toluene and benzene were dissolved in acetonitrile, and reagent **III**, in excess of benzene and toluene mixture at the ratio of concentrations **III**:benzene:toluene = 1:10:10. The reactions were performed in sealed ampules at 80 or 110°C. After the completion of the reaction the ampule was opened, the analysis of the reaction mixtures was performed by ^{19}F NMR. The values f_p and f_m were evaluated by the relative intensity of signals from fluorobenzene, *m*- and *p*-fluorotoluenes in the ^{19}F NMR spectra.

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