SHORT
COMMUNICATIONS
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Comparison of the Reactivity of $R_3\overset{+}{N}F$ Fluorine Carriers as Highly Efficient Fluorinating Agents*

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We previously developed a program for quantitative estimation of solvation effects on the reactivity of fluorinating agents [1–3]. The proposed approach takes into account real experimental conditions and hence ensures higher accuracy of predictions. The fluorinating power is estimated by the heat effect of the model reaction, fluorination of pyridine, with regard to solvation of reactants in solvents of various polarities. An advantage is that fluorine carriers can be compared not only with each other but also with such a classical fluorinating agent as *N*-fluoropyridinium: if the heat effect of the reaction is negative, the fluorine carrier under study is superior to *N*-fluoropyridinium in the fluorinating power and vice versa.

The present communication reports on the relative reactivities of practically interesting and commercially available fluorinating reagents: 4-chloromethyl-1-fluoro-1,4-diazoniabicyclo[2.2.2]octane bis(tetrafluoroborate) (**Ia**), 1-fluoro-4-hydroxy-1,4-diazoniabicyclo[2.2.2]octane bis(tetrafluoroborate) (**IIa**), and isomeric 1,1′- and 4,4′-difluoro-2,2′-bipyridinium salts **IIIa** and **IVa**.

The calculations showed that structurally related compounds **Ia** and **IIa** are characterized by similar solvation parameters (Table 1) and similar fluorinating powers (Table 2), in keeping with the experimental data in [4, 5]. The same conclusion follows from the experimental data on electrochemical reduction of the N−F bond, which is the generally accepted parameter of fluorinating power of N−F reagents: the half-wave reduction potentials of compounds **Ia** and **IIa** almost coincide with each other: $E_{1/2}$ = 0.33 and 0.32 V, respectively [6].

The efficiency of the proposed approach is also illustrated by comparison of the fluorinating powers of compounds **IIIa** and **IVa** in different solvents (Table 2). The first of these is a considerably stronger fluorinating agent than the second. This conclusion is supported by the experimental data: the fluorination of 2-acetylhexanone with compound **IIIa** takes 5 min (yield 85%), and with compound **IVa**, 5 h (87%), other conditions being equal [7].
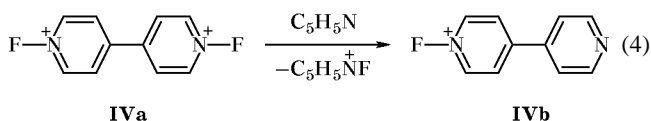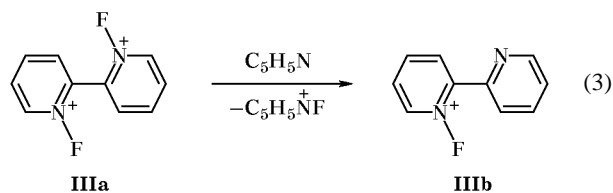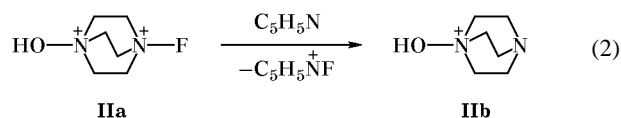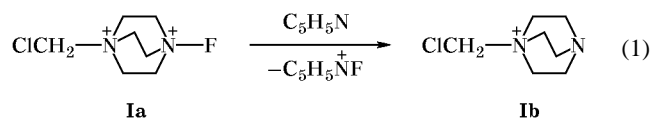
On the whole, our results are consistent with the fact that large-scale products **Ia** and **IIa** are the most powerful fluorinating agents. Commerciably available compounds **IIIa** and **IVa** exhibit a weaker reactivity. Naturally, it should be kept in mind that the final

Table 1. Gas-phase enthalpies of formation $\Delta H(\text{g})$ (kcal/mol) and Gibbs energies $\Delta G(\text{s})$ (kcal/mol) of the reagents and products of reactions (1)–(4) in solvents with different polarities (PM3 calculation data)

Reagent	$\Delta H(\text{g})$ $\varepsilon = 1$	$\Delta G(\text{s})$			
		$\varepsilon = 10$	$\varepsilon = 20$	$\varepsilon = 30$	$\varepsilon = 78$
F$^+$	410.7	318.2	313.1	311.4	309.2
Pyridine	30.4	27.6	27.3	27.2	27.2
N-Fluoro-pyridinium	204.6	153.3	150.3	149.2	148.0
Ia	442.4	271.7	260.9	257.2	252.6
Ib	164.2	117.0	113.7	112.8	111.7
IIa	448.5	270.3	259.1	255.2	250.9
IIb	165.3	115.2	111.6	110.4	109.3
IIIa	487.9	328.2	318.5	315.2	311.2
IIIb	232.9	187.1	184.2	183.1	181.9
IVa	476.1	318.5	309.2	306.1	302.3
IVb	235.7	184.5	181.1	179.9	178.5

Table 2. Heat effects H_{react} (kcal/mol) of reactions (1)–(4) in the gas phase and in solvents with different polarities (PM3 calculations)

Reaction no.	$\varepsilon = 1$	$\varepsilon = 10$	$\varepsilon = 20$	$\varepsilon = 30$	$\varepsilon = 78$
1	–104.0	–28.9	–24.2	–22.4	–20.1
2	–109.0	–29.5	–24.6	–22.8	–20.8
3	–80.7	–15.4	–11.4	–10.0	–8.5
4	–66.2	–8.3	–5.2	–4.2	–3.0

Table 3. Heats of pyridine fluorination with compounds **V** and **VI** in solvents with different polarities (PM3 calculations)

Compound no.	H_{reac}, kcal/mol			
	$\varepsilon = 10$	$\varepsilon = 20$	$\varepsilon = 30$	$\varepsilon = 78$
V	–13.5	–12.8	–13.6	–14.6
VI	9.8	5.8	4.4	2.7

conclusion must be drawn from the kinetic data. Nevertheless, our procedure provides fairly reliable estimation of the relative reactivity of fluorinating agents, so that it may be useful for experimentalists.

From the structural point of view, the fluorinating power strongly depends on the presence of electron-acceptor groups in the molecule of fluorine carrier. Among numerous fluorinating agents there are no compounds containing such a strong activating substituent as nitro group. However, such reagents have been reported, e.g., $[(\text{NO}_2)_3\text{CCH}_2]_2\text{NF}$ (**V**) and $[\text{F}(\text{NO}_2)_2\text{CCH}_2]_2\text{NF}$ (**VI**) [8]. We also estimated their relative reactivity (Table 3). The results showed that N-fluoroamine **V** is characterized by moderate reactivity, and compound **VI** is a weaker fluorinating agent that **V**; in addition, reagents **V** and **VI** are expensive and unstable on exposure to air.

The gas-phase heats of formations ΔH_f of compounds involved in reactions (1)–(4) were calculated by the PM3 method [9] with full geometry optimization using MOPAC program [10]. The optimized geometric parameters were used in the calculations of solvated molecules whose energies were approximated in terms of the Born–Kirkwood–Onsager polarised continuum model (PCM) [11] modified for semi-empirical methods [12].

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