Effect of reaction conditions on the kinetic and activation parameters for the mild introduction of fluorine into α-substituted styrenes with Accufluor™ NFTh

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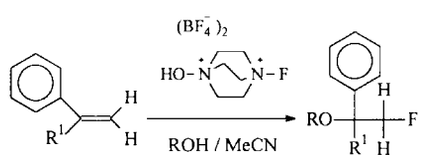
Kinetic studies on fluorination of α-substituted styrenes with 1-fluoro-4-hydroxy-1,4-diazoniabicyclo[2.2.2]octane bis(tetrafluoroborate) (Accufluor™ NFTh) in acetonitrile or in acetonitrile in the presence of methanol or water as nucleophiles were carried out. These reactions exhibited overall second-order kinetics and formed Markovnikov type products. The corresponding second-order rate constants for fluorination of the studied substrates in the presence of methanol at 38.8 °C are: $k_2 = 1.1 \times 10^{-3}$ M^{-1} s^{-1} for styrene (**1a**), 3.3×10^{-2} M^{-1} s^{-1} for α-methylstyrene (**1b**) and 3.4×10^{-2} M^{-1} s^{-1} for 1,1-diphenylethene (**1c**). The substitution of methanol as nucleophile by water had very little effect on the rate of the process. Solvent polarity variation (Grunwald–Winstein Y_{benzyl}) showed a similar small effect, too, indicating negligible change in the polarity of the rate-determining transition state in comparison with the reactants. Activation enthalpies (between 62 and 80 kJ mol^{-1}) and activation entropies (between −74 and −32 J mol^{-1} K^{-1}) were determined for fluorination of α-substituted styrenes with NFTh in acetonitrile in the presence of methanol and water as nucleophiles. Hammett correlation analysis of the reaction of substituted styrenes with NFTh in MeCN, MeCN–H_2O and MeCN–MeOH gave reaction constants ρ^+ of −1.48, −1.52 and −1.80, respectively, which support our belief in the mainly non-polar character of the rate-determining transition state of the studied reactions.

Introduction

The most fundamental information about a chemical reaction is obtained from the study of the nature of the products that are formed during its course. Besides this, chemical kinetics represents a very powerful tool in the hands of a chemist trying to determine the mechanism of the studied reaction. Although fluorination of organic molecules has attracted a great deal of attention from organic chemists in the last three decades, mainly because of the special physicochemical characteristics[1] and the enhanced biological activity of fluorine-containing organic molecules,[2–5] kinetic evaluations in this field are rather scarce.[6–8] This situation, which could in some cases be ascribed to the high reactivity of fluorinating reagents[9–13] (CF_3OF, CF_3COOF, $CsSO_4F$, XeF_2, *etc.*) and the very high sensitivity of these reagents to reaction conditions, may potentially be improved with the introduction of the N–F class of reagents[11,14,15] as optimally reactive, stable, non-explosive and non-expensive reagents for selective introduction of a fluorine atom into organic molecules. Generally, the properties of every new reagent should be studied on model substances. Phenyl-substituted alkenes are excellent target molecules for the study of various electrophilic addition reactions, and they have also often been used in the study of electrophilic fluorinations,[10,13] mainly because they form stable products in fluorination reactions. One member of this group of alkenes is styrene, where it is possible to investigate electronic effects on the reactive intermediates involved in the studied reactions through the introduction of substituents on the aromatic ring, and electronic and steric effects through the binding of various alkyl and aryl groups around the double bond. Styrene **1a** and its α-substituted derivatives (α-methylstyrene **1b** and 1,1-diphenylethene **1c**) have been thoroughly studied in many electrophilic additions, especially in brominations, where they played a crucial role in assessing the multipathway scheme of the reaction.[16–20] We now report the reactions of these model substances with 1-fluoro-4-hydroxy-1,4-diazoniabicyclo[2.2.2]-octane bis(tetrafluoroborate) (Accufluor™ NFTh), known as an effective and selective reagent for mild fluorination of phenyl-substituted alkenes,[21] while its oxidising power enables us to follow these reactions by iodometric titration[22] and thus determinate some kinetic data.

Results and discussion

In our previous report[21] we demonstrated that phenyl-substituted alkenes reacted with NFTh in acetonitrile in the presence of a nucleophile (methanol or water) giving fluoro-methoxy and fluoro-hydroxy adducts, respectively, almost in quantitative yield, with the nucleophile entering the molecule according to the Markovnikov rule (Scheme 1). We have



1a R^1=H **2a** R^1=R=H; **3a** R^1=H, R=Me
1b R^1=Me **2b** R^1=Me, R=H; **3b** R^1=R=Me
1c R^1=Ph **2c** R^1=Ph, R=H; **3c** R^1=Ph, R=Me

Scheme 1

established now that the rates of fluorination of styrene **1a**, α-methylstyrene **1b** and 1,1-diphenylethene **1c** with NFTh in acetonitrile in the presence of a nucleophile follow a simple second order rate equation (1), where L represents the ligand part of the fluorinating reagent to which a reactive fluorine is attached.

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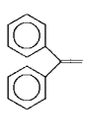
Table 1 The effect of alkene structure (**1**), nucleophile and reaction temperature on the second order rate constants for fluorination with NFTh

Alkene	Nu[a]	T/°C	k_2/M^{-1} s^{-1}	$\Delta G^{\ddagger}$/kJ mol^{-1} [b]	$\Delta H^{\ddagger}$/kJ mol^{-1}	$\Delta S^{\ddagger}$/J mol^{-1} K^{-1}
 **1a**	CH_3OH	42.9	$(1.67 \pm 0.03) \times 10^{-3}$	94 ± 3	75 ± 2	−60 ± 3
		47.5	$(2.95 \pm 0.01) \times 10^{-3}$			
		52.2	$(3.90 \pm 0.01) \times 10^{-3}$			
	H_2O	42.7	$(9.83 \pm 0.07) \times 10^{-4}$	95 ± 3	80 ± 2	−49 ± 2
		48.3	$(1.67 \pm 0.04) \times 10^{-3}$			
		52.2	$(2.46 \pm 0.05) \times 10^{-3}$			
 **1b**	CH_3OH	24.0	$(8.93 \pm 0.04) \times 10^{-3}$	85 ± 2	66 ± 1	−60 ± 1
		29.6	$(1.50 \pm 0.08) \times 10^{-2}$			
		38.8	$(3.4 \pm 0.1) \times 10^{-2}$			
	H_2O	24.0	$(4.84 \pm 0.04) \times 10^{-3}$	86 ± 4	76 ± 4	−32 ± 3
		32.1	$(1.25 \pm 0.09) \times 10^{-2}$			
		40.2	$(2.51 \pm 0.04) \times 10^{-2}$			
 **1c**	CH_3OH	23.5	$(9.05 \pm 0.08) \times 10^{-3}$	85 ± 3	62 ± 2	−74 ± 4
		31.3	$(1.71 \pm 0.08) \times 10^{-2}$			
		38.7	$(3.3 \pm 0.2) \times 10^{-2}$			
	H_2O	23.5	$(6.7 \pm 0.2) \times 10^{-3}$	86 ± 5	74 ± 4	−37 ± 3
		31.1	$(1.39 \pm 0.02) \times 10^{-2}$			
		38.3	$(2.72 \pm 0.01) \times 10^{-2}$			

[a] The ratio of Nu : MeCN = 1 : 11. [b] Calculated from the equation $\Delta G^{\ddagger} = \Delta H^{\ddagger} - T\Delta S^{\ddagger}$ for T = 38.8 °C.

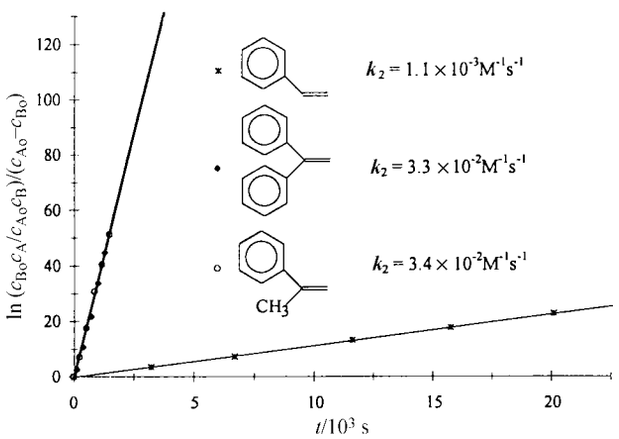


Fig. 1 Effect of alkene structure on fluorination with NFTh in MeCN–MeOH at 38.8 °C for styrene (**1a**), α-methylstyrene (**1b**) and 1,1-diphenylethene (**1c**).

$$d[F\text{–}L]/dt = k_2[F\text{–}L][\mathbf{1}] \quad (1)$$

As is evident from Fig. 1 the introduction of the substituent on the α position into styrene **1a** has an accelerating effect on the reaction, but surprisingly, the nature of the substituent has practically no effect on the reaction rate. In the case of methyl and phenyl substituents in the α position, the enhancement of the rate of reaction is a factor of 30 at 38.8 °C for fluorination with NFTh in acetonitrile in the presence of methanol.

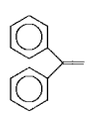
Further, we compared the second order rate constants for fluorination of styrene **1a** at 52 °C and both α-substituted substrates **1b** and **1c** at 24 °C in the presence of various nucleophiles and the results are presented in Table 1. We found that in the case of fluorination of styrene the second order rate constant is a factor of 1.6 smaller in the presence of water than in the presence of methanol, while the reaction of α-methylstyrene **1b** is slowed down by a factor of 1.8 in the presence of water. The retardation of the fluorination of 1,1-diphenylethene **1c** in the presence of water is even smaller, by a factor of 1.3.

The determination of the second order rate constants for fluorination of all three substrates **1a**–**1c** at various temperatures in the presence of both nucleophiles also enabled us to determine the activation parameters for these reactions, which give us additional information about the nature of the rate-determining transition state. Inspection of the data gathered in Table 1 reveals some interesting facts. The values of the activation free energies ($\Delta G^{\ddagger}$) for fluorination of all three substrates (**1a**, **1b**, **1c**) differ only slightly in the presence of different nucleophiles. However, we found that activation enthalpies ($\Delta H^{\ddagger}$) are lower in the presence of methanol for all three substrates, while the values of activation entropies ($\Delta S^{\ddagger}$) are higher in the presence of water, thus compensating for more unfavorable values of activation enthalpies ($\Delta H^{\ddagger}$) in this medium, which implies differences in the structure of the rate-determining transition states in the presence of various nucleophiles. The more negative values of activation entropies ($\Delta S^{\ddagger}$) and lower values of activation enthalpies ($\Delta H^{\ddagger}$) in the presence of methanol indicate the relatively more organised structure of the rate-determining transition state, with bond formation and charge development a little more advanced than in the presence of water.

Valuable information about the structure of the rate-determining transition state for the fluorination of phenyl-substituted alkenes with NFTh could be obtained from the study of the effect of the change in the solvent polarity on the rate of the reaction. Unfortunately, fluorine introduction is quite solvent dependent, and even small changes in this reaction parameter could completely stop the process or alter its course. This reaction proceeds really well only in acetonitrile and in acetonitrile in the presence of a nucleophile, so for this study we used acetonitrile–water mixtures where Grunwald–Winstein values (Y)[23] (as one of the possible measures of the solvent polarity) have already been determined and fortunately found to have a very large range.[24] Considering the data from Table 2 it is obvious that even large variations in Y have only a small effect on the rate of fluorination of styrene **1a**, α-methylstyrene **1b** and 1,1-diphenylethene **1c**, indicating a small change in the polarity of the rate-determining transition state in comparison with the reactants. It is well known that in the case of *e.g.* bromination of methylideneadamantane[25] and solvolysis of *p*-methoxybenzyl chloride,[26] known as predominantly polar reactions, the effect of the change in the solvent polarity on the rate of reaction is considerable (Fig. 2).

As part of our continuing investigations into the nature of the rate-determining state and intermediate formed in this step, we extended our study to the examination of the substituent effects on the kinetic parameters of fluorination of styrenes. First, we performed Hammett correlation analysis for the fluorination of the substituted styrenes with NFTh in acetonitrile without an added nucleophile. The products formed in this reaction were already identified as vicinal fluoroacetamides,[27] except in the case of *p*-methoxystyrene, where even a trace amount of water resulted in the formation of a vicinal hydroxy-fluoride with Markovnikov-type regioselectiv-

Table 2 Effect of solvent polarity on the second order rate constants for fluorination of α-substituted-styrenes (**1a**) in acetonitrile–water solution

Substrate	Solvent	T/°C	Y_{benzyl} [a]	$10^3\ k_2/M^{-1}\ s^{-1}$	log k_2	m
	90% MeCN		−1.45	2.20 ± 0.01	−2.7	
	80% MeCN	52.0	−0.35	1.25 ± 0.02	−2.9	−0.21
	60% MeCN		0.81	0.73 ± 0.02	−3.1	
1a						
	90% MeCN		−1.45	4.9 ± 0.3	−2.3	
	80% MeCN	25.0	−0.35	2.60 ± 0.06	−2.6	−0.20
	60% MeCN		0.81	1.7 ± 0.1	−2.8	
1b						
	90% MeCN		−1.45	4.62 ± 0.01	−2.3	
	80% MeCN	25.0	−0.35	2.05 ± 0.05	−2.7	−0.27
	60% MeCN		0.81	1.05 ± 0.01	−3.0	
	40% MeCN		1.74	0.62 ± 0.01	−3.2	
1c						

[a] See ref. 24.

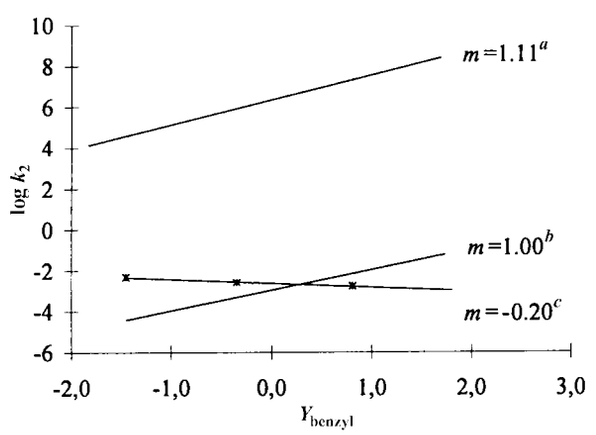
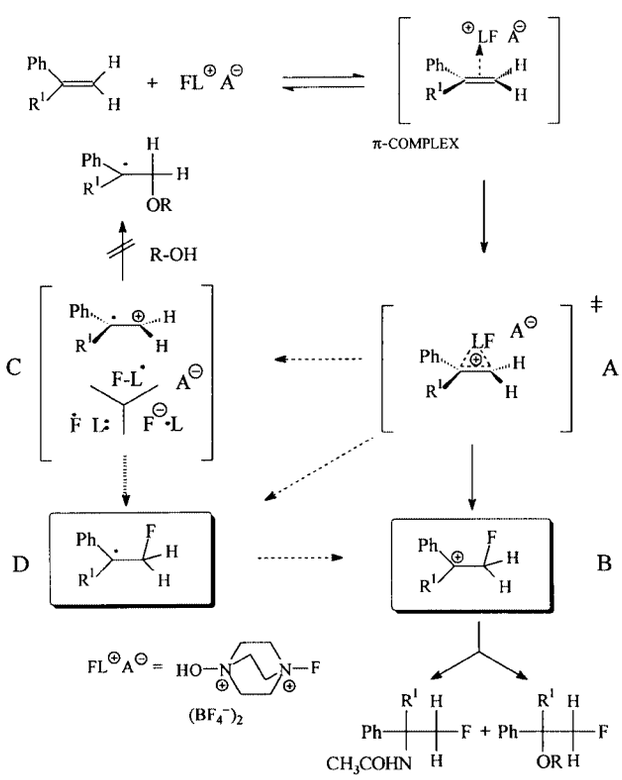


Fig. 2 Comparison of the effect of solvent polarity (Y_{benzyl} [24]) on the rate of fluorination of α-methylstyrene (**1b**) and the rate of some ionic reactions.[25,26] [a] Bromine addition to methylideneadamantane, ref. 25. [b] Solvolysis of *p*-methoxybenzyl chloride, ref. 26. [c] Fluorination of **1b** with NFTh in MeCN–H_2O at 25.0 °C.

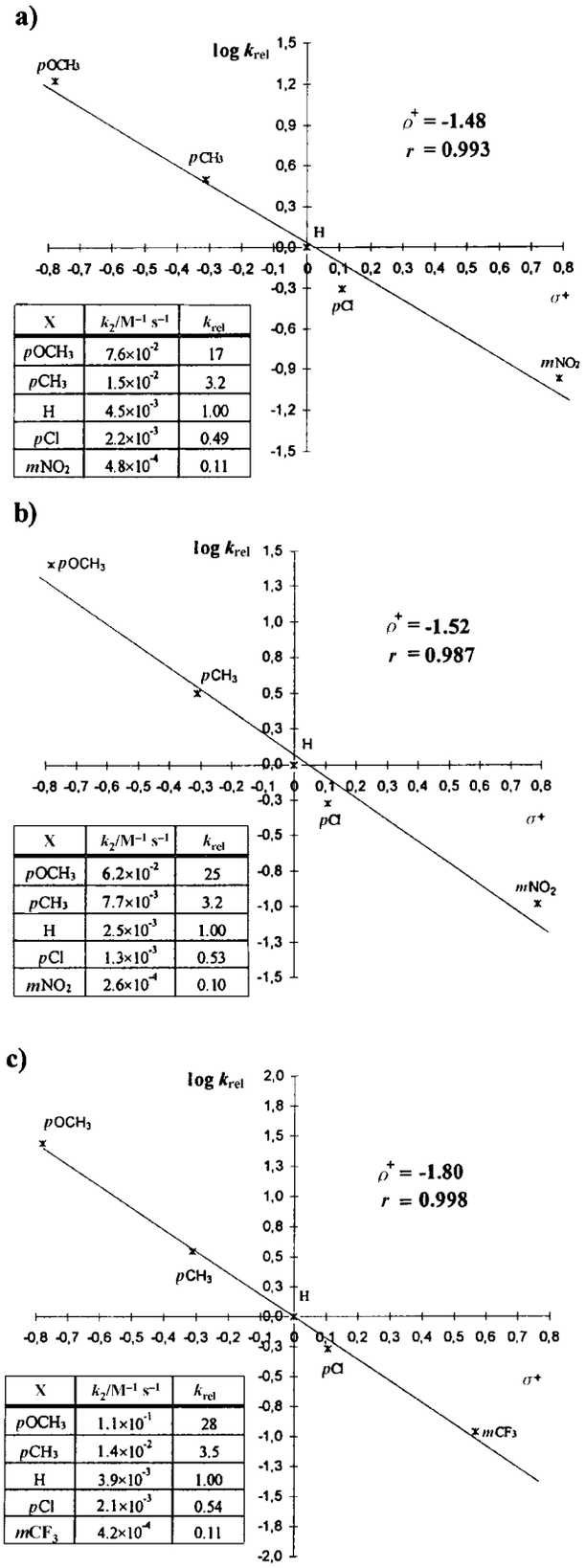
ity. From the measured second order rate constants k_2 we calculated the relative constants of the rates of fluorination k_{rel} and from the correlation of these factors with electrophilic substituent constants σ^+ we determined the reaction constant ρ^+ as −1.48 with a correlation coefficient of 0.993 (Fig. 3a). The correlation analysis for the fluorinations of substituted styrenes with NFTh in acetonitrile in the presence of water and methanol gave the reaction constants ρ^+ of −1.52 and −1.80, respectively (Fig. 3b and 3c). Product distribution in these reactions was as expected, as with more reactive substrates only vicinal hydroxy- and methoxy-fluorides were formed,[21] but we additionally found that in the case of less reactive substrates these products were accompanied by vicinal fluoroacetamides, their relative ratio increasing from a trace amount in the case of styrene to 50% in the case of *m*-nitrostyrene. A comparison of our reaction constants with ρ values for other addition reactions involving substituted styrenes helps us in establishing the structure of the rate-determining transition state. For instance, for acid catalysed hydration of styrenes,[28] where $\rho^+ = -3.58$ was determined, the proposed structure of the transition state was an opened, unsymmetrical cation, while in the case of methoxymercuration of substituted styrenes[29,30] with $\rho = -3.16$ and $\rho^+ = -2.76$ an unsymmetrically bridged ion[29,30,31] was mentioned as the most probable structure of the rate-determining transition state. The reaction constant $\rho = -2.20$, determined for the reaction of *p*-substituted styrenes with 2,4-dinitrobenzenesulfenyl chloride which proceeds through a symmetrically bridged episulfonium ion,[32] is so far the value closest to our reaction constants, as is in accordance with our prediction of a symmetrically bridged, largely non-polar structure for the rate-determining transition state. It is demonstrated once again that charge development in the rate-determining step of fluorination is the most advanced in the fluorination of substituted styrenes in the presence of methanol.

On the basis of all the data gathered and presented in this article, we are now able to suggest a reaction mechanism for the mild fluorination of substituted styrenes with NFTh, an "electrophilic" fluorinating agent, in acetonitrile in the presence of a nucleophile (Scheme 2).



Scheme 2

First, it seems obvious that the rate-determining transition state **A** has a mainly nonpolar nature, and is most likely formed through a π-complex between the reagent and substrate. This proposed mechanistic scheme is supported by the established small effect of changes of solvent polarity on the rate of reac-



X	k_2/M^{-1} s^{-1}	k_{rel}
pOCH$_3$	7.6×10^{-2}	17
pCH$_3$	1.5×10^{-2}	3.2
H	4.5×10^{-3}	1.00
pCl	2.2×10^{-3}	0.49
mNO$_2$	4.8×10^{-4}	0.11

X	k_2/M^{-1} s^{-1}	k_{rel}
pOCH$_3$	6.2×10^{-2}	25
pCH$_3$	7.7×10^{-3}	3.2
H	2.5×10^{-3}	1.00
pCl	1.3×10^{-3}	0.53
mNO$_2$	2.6×10^{-4}	0.10

X	k_2/M^{-1} s^{-1}	k_{rel}
pOCH$_3$	1.1×10^{-1}	28
pCH$_3$	1.4×10^{-2}	3.5
H	3.9×10^{-3}	1.00
pCl	2.1×10^{-3}	0.54
mCF$_3$	4.2×10^{-4}	0.11

Fig. 3 Hammett correlation plot (log k_{rel}/σ^+) for fluorination of substituted styrenes with NFTh in various solvents. a) Fluorination in acetonitrile. b) Fluorination in acetonitrile–water (11 : 1) mixture. c) Fluorination in acetonitrile–methanol (11 : 1) mixture.

tion and the low values of the reaction constant ρ^+ (−1.48, −1.52, −1.80), as well.

This rate-determining transition state is presumably further transformed into the β-fluorocarbonium ion **B**. Several facts speak in favour of the proposed opened structure of the reactive intermediate. The most powerful argument for the carbocation intermediate structure is the observed regioselectivity, where the nucleophile or acetonitrile enters the molecule of the substrate with Markovnikov-type regioselectivity, while in the case of reactions which proceed through radical intermediates the opposite regioselectivity was observed[33,34] (as in the case of laser flash photolysis generated ion–radicals from styrene and its substituted derivatives, where the attack of a nucleophile at position C-2 is clearly indicated as the primary process, which is both very dependent on the structure of the nucleophile and also on the steric arrangement at C-2). An additional argument for the opened structure of the β-fluorocarbonium intermediate has also been presented in one of our previous studies,[27] where the formation of fluoroacetamides from alkenes and phenyl-substituted alkenes, which give less stable intermediates with NFTh in acetonitrile, was reported. We also observed recently that in the reaction of F-TEDA {F-TEDA = 1-(chloromethyl)-4-fluoro-1,4-diazoniabicyclo[2.2.2]octane bis(tetrafluoroborate)} with norbornene rearranged products were formed, suggesting the carbonium ion nature of the intermediate,[35] while a photochemically generated norbornene ion–radical reacted with a nucleophile forming a radical intermediate and no rearranged products were observed.[36]

However, the discussion of the possible mechanisms of fluorination of organic compounds with "electrophilic" fluorinating agent is still far from closed, as we are not able to clearly discriminate between two possible pathways of formation of the intermediate, namely direct fluorine transfer and a two-step pathway with cation–radical intermediates, which has been suggested many times in the case of the mild introduction of fluorine into phenyl-substituted alkenes with the N–F type of reagents to be the main reaction path.[14,15,37,38] Although, on the basis of the present data, we propose direct formation of the β-fluorocarbonium ion, the formation of cation–radicals, and thus one electron transfer, could not be completely excluded, especially as we do not have enough information about the structure of the electron-accepting species (F–L$^{\bullet}$ or F^{-}L$^{\bullet}$ or :L F$^{\bullet}$). For this reason we also included the possibility of the formation of a cation–radical and an anionic part of the fluorinating agent pair **C** in the proposed mechanistic scheme, which could be further transformed into the radical intermediate **D**, and in the next very fast step, the β-fluorocarbonium intermediate **B**. The alternative reaction of the proposed pair **C** with alcohol or water is not an option.

Experimental

1-Fluoro-4-hydroxy-1,4-diazoniabicyclo[2.2.2]octane bis(tetrafluoroborate) (NFTh) was obtained from commercial sources and crystallised from a water–methanol mixture before use. Styrene (Fluka), α-methylstyrene (Aldrich), 1,1-diphenylethene (Aldrich), *p*-methoxystyrene (Aldrich), *p*-methylstyrene (Aldrich), *p*-chlorostyrene (Aldrich), *m*-nitrostyrene (Aldrich) and *m*-trifluoromethylstyrene (Aldrich) were also obtained from commercial sources and distilled before use. Acetonitrile (Merck) and methanol (Merck) were purified by distillation and stored over molecular sieves. KI (Merck) and a standard solution of $Na_2S_2O_3$ (Riedel-de-Haen) were used as received.

Determination of second order rate constants for fluorination of α-substituted styrenes with NFTh

Various amounts (1.2 mmol or 0.6 mmol) of substrate (styrene (**1a**), α-methylstyrene (**1b**), 1,1-diphenylethene (**1c**) and substituted styrene (*p*-methoxy, *p*-methyl, *p*-chloro, *m*-nitro and *m*-trifluoromethyl)) were dissolved in a thermostatted mixture (at 24, 38.8 or 52.0 °C) of 40 mL of acetonitrile or of 35 mL of acetonitrile and 5 mL of methanol or 5 mL of water, then 20 mL of a thermostatted acetonitrile solution of NFTh (0.6 mmol) were added and the reaction mixture further stirred at the selected temperature. The progress of NFTh consumption

was monitored by iodometric titration and at various times 10 mL aliquots of reaction mixture were mixed with 20 mL of ice cold 0.02 M KI and the liberated iodine was titrated with 0.05 M $Na_2S_2O_3$. Second order rate constants were calculated from eqn. (2), and are gathered in Table 1. In eqn. 2, c_{A_0} and c_{B_0} are

$$\ln(c_{B_0}c_A/c_{A_0}c_B)/(c_{A_0} - c_{B_0}) = k_2t \qquad (2)$$

the initial concentrations of the reagent (NFTh) and the substrate (styrene), respectively; c_A and c_B are the concentrations of the reagent and substrate, respectively, after time t.

For the Hammett correlation plots relative rate factors k_{rel} for substituted styrenes were calculated from k_2 values and are presented in Fig. 3.

Determination of thermodynamic parameters for fluorination of styrene (1a), α-methylstyrene (1b) and 1,1-diphenylethene (1c) with NFTh in the presence of methanol or water

0.6 mmol or 1.2 mmol of substrate was dissolved in 40 mL of acetonitrile or in a mixture of 35 mL of acetonitrile and 5 mL of methanol or water, solutions were thermostatted at three different temperatures for each substrate and 20 mL of a thermostatted acetonitrile solution of NFTh (0.6 mmol) were added. The reaction mixture was stirred and the progress of NFTh consumption was monitored by iodometric titration. A linear correlation between k_2 and temperature was observed and activation parameters were calculated by linear regression from eqn. (3). Results are presented in Table 1.

$$\ln(k_2/T) = \ln(k_b/h) + \Delta S^{\ddagger}/R - \Delta H^{\ddagger}/RT \qquad (3)$$

Influence of solvent polarity on second order rate constant in fluorination of styrene (1a), α-methylstyrene (1b) and 1,1-diphenylethene (1c) with NFTh

1.2 mmol of substrate were dissolved in 40 mL of acetonitrile–water mixture (acetonitrile + water = 34 mL + 6 mL, 28 mL + 12 mL and 16 mL + 24 mL) and thermostatted at 52.0 °C (for **1a**) and 25.0 °C (for **1b** and **1c**), then 20 mL of a thermostatted acetonitrile solution containing 0.6 mmol NFTh were added and stirred. The progress of NFTh consumption was monitored by iodometric titration. The results are presented in Table 2 and Fig. 2.

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