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Kinetic investigations of the reactions of hindered phenols with *N*-fluoro-1,4-diazoniabicyclo[2.2.2]octane salt analogues

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ABSTRACT: The kinetics of reactions of hindered phenols (2,4,6-trimethylphenol, 2,6-di-*tert*-butyl-4-methylphenol and 2,4,6-tri-*tert*-butylphenol) with 1-fluoro-4-chloromethyl-1,4-diazoniabicyclo [2.2.2]octane bis(tetrafluoroborate) (Selectfluor™, F-TEDA-BF_4) in acetonitrile in the absence or presence of various sources of external nucleophile (alcohols, water, trifluoroacetic acid) were studied. The reactions exhibited overall second-order kinetics, whereas products formation was strongly dependent on reaction conditions. Fluorination took place in neat MeCN; in the presence of water or alcohols, *para* quinols or *para* quinol ethers were formed exclusively; under acidic conditions (TFA), Ritter-type amidation was found to be the predominant process. Values for second-order rate constants k_2 were found to be dependent on the structure of the target phenol and decreased with bulkiness of the substrate. Methanol slightly increased the rate, whereas water decreased it considerably. Activation enthalpies (between 72 and 78 kJ mol^{-1}) and activation entropies (between −5 and −42 J mol^{-1} K^{-1}) were obtained. Activation entropies were found to be higher for less-hindered substrates, indicating that the rate-determining steps were mainly regulated by steric factors. Grunwald–Winstein correlation of log k_2 with solvent ionizing power *Y* revealed a relatively small correlation factor *m*. An electron-transfer-type process following the rate-determining formation of substrate–reagent complex was postulated as the key step of the reaction pathway. Copyright © 2001 John Wiley & Sons, Ltd.
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KEYWORDS: hindered phenols; kinetics; *N*-fluoro-1,4-diazoniabicyclo[2.2.2]octane salts; electron transfer

INTRODUCTION

The introduction, followed very soon after by the extensive application, of organic molecules incorporating a reactive N—F bond as versatile mild fluorinating reagents[1] over the last decade has resulted in intensive research into the chemistry of organofluorine molecules.[2] Derivatives of *N*-fluoro-1,4-diazoniabicyclo[2.2.2]octane salts became, very soon after their promotion,[3] one of the most popular groups of these compounds. Being easily handled, cost-effective reagents possessing optimal stability/reactivity characteristics, they are widely used for routine laboratory work as well as for large-scale applications for selective fluorofunctionalization of organic compounds.[1,4] Their oxidative power is among the highest in the N—F reagent series,[5] so one could expect a certain competition between fluorination and oxidation processes, particularly when oxidizable functional groups or heteroatoms are present in the target molecule. Phenols carry a great deal of this potential oxidation/fluorofunctionalization competitive dualism, and this fact was found to be advantageous in their selective transformation with N—F reagents.[6,7]

As part of our continuing interest in the reaction of N—F reagents with phenols, we now report the reactions of sterically hindered phenols with 1-fluoro-4-chloromethyl-1,4-diazoniabicyclo[2.2.2]octane bis(tetrafluoroborate) (**2a**, Selectfluor™, F-TEDA-BF_4) and its 4-hydroxy analogue (**2b**, Accufluor™, NFTh). We have focused on their kinetic evaluation and mechanistic elucidation in order to reach general conclusions about the reaction of N—F reagents with organic molecules.

RESULTS AND DISCUSSION

In a typical experiment 2,6-di-*tert*-butyl-4-methylphenol (**1a**, Scheme 1) was treated with a 10% molar excess of F-TEDA-BF_4 (**2a**) or NFTh (**2b**) in acetonitrile at 10 °C. A

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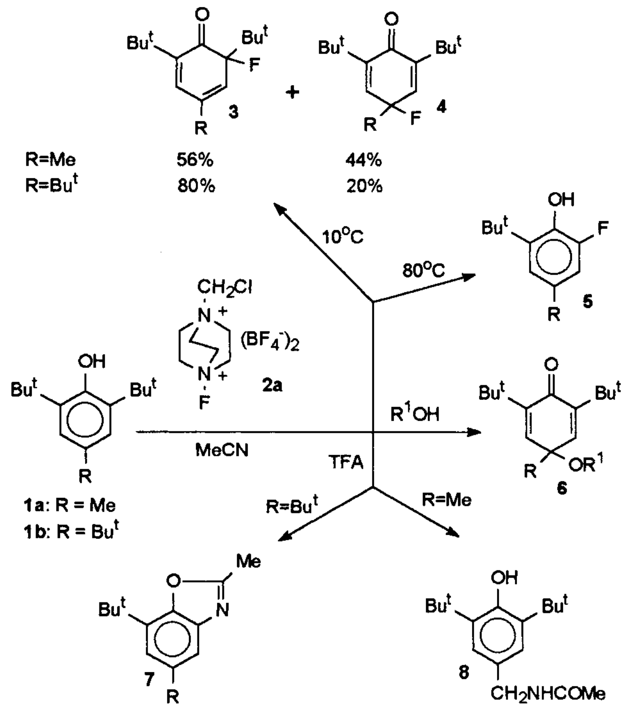
mixture of 2-fluoro-2,6-di-*tert*-butyl-4-methyl-cyclohexa-3,5-dienone (**3a**) and 4-fluoro-2,6-di-*tert*-butyl-4-methyl-cyclohexa-2,5-dienone (**4a**) was isolated in nearly equimolar proportions in over 80% overall yield. At 80 °C the course of the reaction was found to be quite different and 2-fluoro-4-methyl-6-*tert*-butylphenol (**5a**) was formed almost quantitatively, whereas at room temperature all three products were detected in the crude reaction mixture. It appears that the formation of fluoro-substituted cyclohexadienone-type products (**3** and **4**) is characteristic for the reactions of phenols with N—F reagents,[6,7] and that this process is kinetically controlled, whereas fluoro-dealkylation gave the thermodynamically more stable product **5** and is the sole transformation at higher reaction temperature.

The presence of an external nucleophile plays an important role in reactions of N—F reagents with non-aromatic unsaturated organic molecules[1] and, as elaborated previously,[7] the reactions of F-TEDA-BF_4 or NFTh with phenols **1** in the presence of alcohols or water proved an excellent method for the efficient synthesis of *para* quinols or *para* quinol ethers **6**. However, the presence of the more acidic nucleophile-like trifluoroacetic acid (TFA) caused quite different transformations of target phenols **1**. The reaction of **1a** with reagents **2a** and **2b** in acetonitrile in the presence of 10% of TFA resulted in the formation of 2,6-di-*tert*-butyl-4-methylacetamidophenol (**8**, Scheme 1) as the main product (70%), accompanied by small amounts of ring and side-chain trifluoroacetoxy- and/or acetamido-substituted phenols. The similar reaction of 2,4,6-tri-*tert*-butylphenol (**1b**) gave 2-methyl-5,7-di-*tert*-butylbenzoxazole (**7**) as the main product (65%), accompanied by small amounts of 2- and 4-acetamido derivatives of di-*tert*-butylphenol, 2,6-di-*tert*-butylquinone, various isomers of trifluoroacetoxy-substituted derivatives and *N*-*tert*-butylacetamide. It is obvious that, under these conditions, reaction intermediates, rather than collapse with TFA as external nucleophile or with fluorine atom species, reacted with the solvent following a Ritter-type[8] reaction as the main process. The reaction of 2,4,6-trimethylphenol with **2** under acidic reaction conditions was found to be even more complex, and a non-reproducible reaction mixture of more than ten products was isolated, among which various isomers of methylacetamido phenols, di-methyl-acetamido phenols, methylhydroxy-substituted benzyl-phenyl ether derivatives and even trimers of target phenol were identified by gas chromatography–mass spectrometry.

Besides analysis of the products formed, more fundamental information about a chemical reaction may be obtained from its kinetics data. Kinetic evaluation of the reactions of organic molecules with electrophilic fluorinating reagents (XeF_2, fluoroxy and N—F reagents) is rather scarce,[9] mainly due to the high reactivity of these reagents and the high sensitivity of their reactions to reaction conditions. Many of these difficulties can be avoided in the case of certain N—F reagents, whose reaction can be followed by iodometric titration,[10] which allows many valuable kinetic parameters for reactions of N—F reagents with some aromatics[11] and phenyl-substituted alkenes[12] to be obtained.



Scheme 1

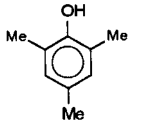
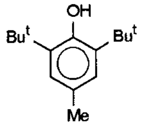
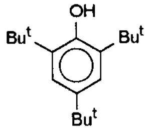
First, we have monitored the consumption of F-TEDA-BF_4 iodometrically during its reaction with different relative concentrations of phenols **1** or 2,4,6-trimethylphenol in MeCN at $T = 15\,°\mathrm{C}$. The reaction rates have been shown to obey the simple second-order rate equation

$$\mathrm{d}[\text{F-TEDA-BF}_4]/\mathrm{d}t = k_2[\text{F-TEDA-BF}_4]\ [\text{phenol}] \quad (1)$$

in the case of all three target molecules, indicating that the rate-determining step is bimolecular. We obtained the following values for second-order rate constants k_2 for the reactions of target phenols with F-TEDA-BF_4 in MeCN at 15 °C: $3.5 \times 10^{-2}\,\mathrm{M}^{-1}\,\mathrm{s}^{-1}$ for the 2,4,6-trimethylphenol; $1.5 \times 10^{-2}\,\mathrm{M}^{-1}\,\mathrm{s}^{-1}$ for 2,6-di-*tert*-butyl-4-methylphenol; $9.0 \times 10^{-3}\,\mathrm{M}^{-1}\,\mathrm{s}^{-1}$ for 2,4,6-tri-*tert*-butylphenol. The least hindered target phenol is thus four times more reactive than the most hindered one. From the data, collected in Tables 1 and 2, it can be seen that the presence of the external nucleophile has a certain effect on the reaction rate. The effect of methanol on the second-order rate constants for all three phenols is relatively small (entries 2, 7 and 9, Table 1), whereas ethylene glycol (entries 5 and 13 Table 1) and water (Table 2) decreased it considerably.

Activation parameters for the reactions mentioned

Table 1. The effects of substrate structure and of external nucleophile on the second-order rate constant k_2 and activation parameters for the reactions of hindered phenols with Selectfluor®, F-TEDA-BF_4, in acetonitrile at 15 °C

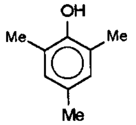
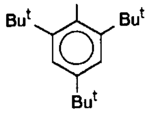
Entry	Phenol	NuH[a]	NuH:MeCN	k_2 (M^{-1} s^{-1})	$\Delta G^{\#}$ (kJ mol^{-1})	$\Delta H^{\#}$ (kJ mol^{-1})	$\Delta S^{\#}$ (J mol^{-1} K^{-1})
1		H_2O	1:9	2.7×10^{-2}	79 ± 1	77 ± 1	−8.3 ± 0.5
2		MeOH	1:9	3.2×10^{-2}	79 ± 2	77 ± 1	−5.0 ± 0.1
3		MeOH	2:8	3.8×10^{-2}			
4		MeOH	4:6	4.3×10^{-2}			
5		$HOCH_2CH_2OH$	1:9	2.0×10^{-2}	80 ± 2	75 ± 1	−17 ± 1
6		H_2O	1:9	6.1×10^{-3}			
7		MeOH	1:9	1.3×10^{-2}	81 ± 2	75 ± 1	−19 ± 1
8		CF_3CO_2H	1:9	1.5×10^{-2}	81 ± 2	78 ± 2	−10 ± 1
9		H_2O	1:9	4.1×10^{-3}	84 ± 2	72 ± 1	−41 ± 1
10		MeOH	1:9	8.2×10^{-3}	82 ± 2	73 ± 1	−33 ± 1
11		MeOH	2:8	8.2×10^{-3}			
12		MeOH	4:6	9.8×10^{-3}			
13		$HOCH_2CH_2OH$	1:9	4.5×10^{-3}	83 ± 1	75 ± 1	−29 ± 1
14		CF_3COOH	1:9	1.2×10^{-2}	81 ± 2	73 ± 2	−25 ± 1

[a] NuH: source of nucleophile.

were determined from the dependence of second-order rate constant on temperature, which gives us additional information about the nature of the rate-determining transition state. The activation free energy $\Delta G^{\#}$ for these reactions had values of around 80 kJ mol^{-1} at 15 °C for all three substrates (Table 1), independent of the structure of the external nucleophile. The effect of the structure of target phenols on activation enthalpies $\Delta H^{\#}$ was also small for all three substrates, and the activation entropies $\Delta S^{\#}$ depended considerably on the structure of the target phenol as well as on the presence of external nucleophile. The value of $\Delta S^{\#}$, under comparable reaction conditions, was higher in the case of 2,4,6-trimethylphenol than for **1a** or **1b**, indicating a much less organized structure of the rate-determining transition state in comparison with the sterically much more hindered 2,6-di-*tert*-butyl-substituted substrates. This is reasonable, since sterically more-hindered phenols are expected to demand a more organized transition state in order to initiate a flow of electrons.

The dependence of the second-order rate constant on the concentration of external nucleophile varied, an increase in methanol making the reaction slightly faster, whereas water slowed it down (Table 2). The latter observation was evaluated using a Grunwald–Winstein[13] correlation of log k_2 with values of solvent ionizing

Table 2. Effect of solvent polarity on kinetic and activation parameters of the reaction of phenols with Selectfluor®, F-TEDA-BF_4, in acetonitrile/water solution

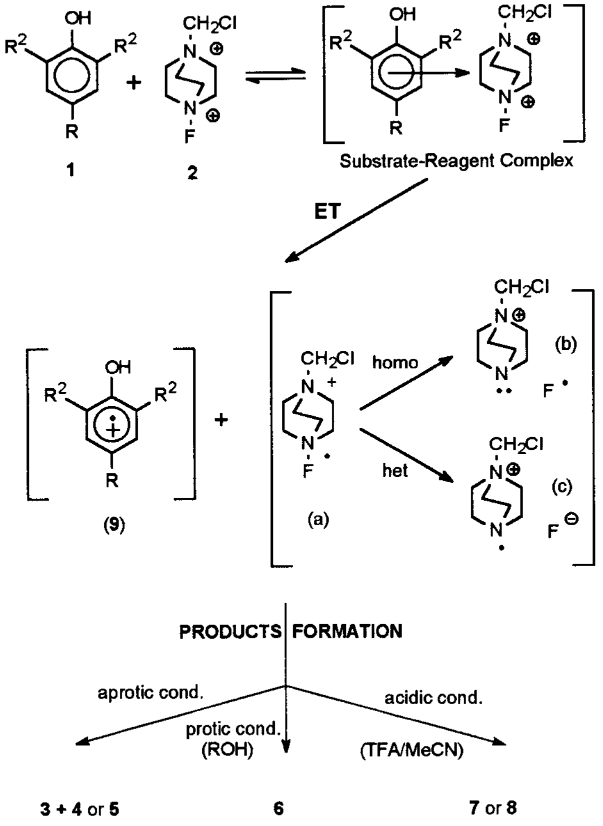
Entry	Phenol	H_2O in MeCN (%)	T (°C)	k_2 (M^{-1} s^{-1})	$\Delta G^{\#}$ (kJ mol^{-1})	$\Delta H^{\#}$ (kJ mol^{-1})	$\Delta S^{\#}$ (J mol^{-1} K^{-1})	Y^a	m
1		10	15.0	2.7×10^{-2}	79 ± 1	77 ± 3	−8.3 ± 0.4	−1.45	
2		20	15.0	2.3×10^{-2}				−0.35	
3		30	15.0	2.0×10^{-2}				0.22[b]	−0.08
4		40	14.9	1.9×10^{-2}				0.81	
5		10	15.0	4.4×10^{-3}	84 ± 2	72 ± 1	−41 ± 1	−1.45	
6			20.0	7.6×10^{-3}					
7			25.0	1.2×10^{-2}					
8			30.0	2.1×10^{-2}					
9		20	15.0	2.8×10^{-3}	85 ± 1	73 ± 1	−42 ± 1	−0.35	
10			20.0	4.8×10^{-3}					−0.18
11			30.0	1.3×10^{-2}					
12			35.0	2.1×10^{-2}					
13		22.5	30.1	1.2×10^{-2}				−0.16[b]	
14		25	30.0	1.1×10^{-2}				−0.04[b]	

[a] Y values for MeCN/water mixture obtained from Ref. 14.

[b] Interpolated values.

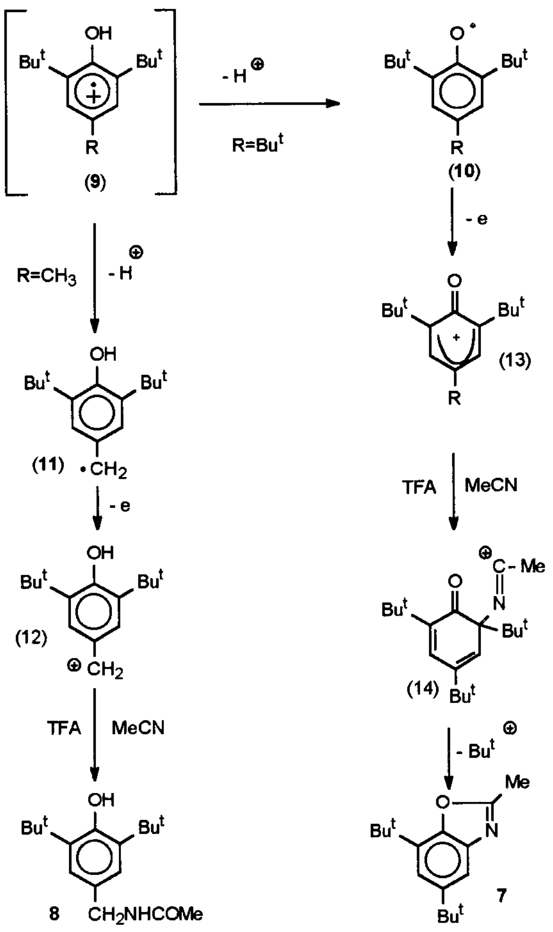
power *Y*, a measure of solvent polarity. The relatively small correlation factor *m* obtained indicates only a small change in the polarity of the rate-determining transition state compared with the reactants.

The mechanism of reaction of ‘electrophilic’ fluorinating reagents with organic molecules is still open to discussion, but it has been generally accepted that the course of these reactions is strongly dependent on the structure of the reagent and the target molecule, as well as on reaction conditions. Unequivocal definition of the reaction pathway through which the products are formed is very difficult, but two boundary concepts were accepted. The main postulate of the first concept is a transfer of a fluorine atom (FT) through a classical S_N2 process: an electron-rich reaction centre on the target molecule attacks the fluorine atom on a reagent, displacing its ligand part, which must necessarily be a better leaving group than fluoride. The second concept accepts electron transfer (ET) as the key process in these reactions. It postulates the initial formation of a charge-transfer complex between an electron-rich organic molecule and an electron-deficient fluorinating reagent, followed by one-electron transfer, thus forming a target molecule cation radical as the active intermediate and precursor of fluorinated or non-fluorinated products.[1] The formation of a charge-transfer complex and cation radical intermediates was demonstrated by UV spectroscopy in the case of reactions of activated aromatics with *N*-fluoropyridinium salts,[15] and cation radicals were monitored by electron spin resonance spectroscopy in the case of reactions of *N*-halogen reagents (NBS or NCS) with electron-rich aromatics.[16]



Scheme 2

On the basis of the present results, we conclude that the reaction pathway in the reactions of F-TEDA-BF$_4$ or NFTh with hindered phenols involves an electron-transfer process. The most probable reaction pathways leading to the products observed are shown in Schemes 2 and 3. The initial substrate–reagent complex, after electron transfer from donor phenol **1** to acceptor F-TEDA-BF$_4$, gives a cation-radical (**9**, Scheme 2) and an N—F radical species [(a), Scheme 2]. This species could disproportionate by a homolytic (b) or heterolytic (c) process, thus revealing $F^{\cdot}$ or F^-, and all three of them could be the potential fluorine atom transfer carriers. The transformation of cation-radical (**9**) to the products is crucially affected by the reaction conditions, and we observed the formation of three main types of product. Under aprotic conditions (neat MeCN), the fluorination of target molecules, resulting in 2- and 4-fluoro-substituted cyclohexadienone derivatives (**3** and **4**) or 2-fluoro-substituted phenols (**5**), was the exclusive process, whereas under protic conditions (MeCN and 10% ROH) regiospecific formation of *para* quinols or *para* quinol ethers (**6**) took place. The third process, Ritter-type amidation of target molecules, was found to be the main transformation under acidic conditions (MeCN and 10% TFA), which is usually the case in these kinds of transformation.[8] TFA also plays a significant role in the persistence of radical cations,[17] which, as highly acidic species, readily release a proton.[15b] Radical cation (**9**) thus transforms by proton loss to a phenoxy (**10**) or benzyl radical (**11**), which, immediately after another electron transfer, yields benzyl cation (**12**) in the case of **1a** or cyclohexadienone cation (**13**) in the case of **1b**. Ritter-type collapse of **12** with MeCN solvent resulted in *para*-methylacetamido phenol **8**. In the second case an *ortho* attack of MeCN to **13**, followed by cyclization and dealkylation of intermediate **14** to the benzooxazole derivative **7**, is the driving force of the reaction (Scheme 3). The direct attack of MeCN to radical cation **9** is also optional in the case of the formation of the product **7**, as observed recently elsewhere.[18] Which of the reaction steps in Scheme 2 is rate determining depends, among others factors, on the ionisation potentials (IPs) and half-wave redox potentials $E_{1/2}$ of the target phenols. If the electron-transfer process is rate determining, then, with increasing IP or $E_{1/2}$, the reaction rate would be expected to decrease. Although IP and $E_{1/2}$ values increase from **1b** through **1a** to 2,4,6-trimethylphenol,[19] and second-order rate constants increase in the opposite direction, these differences are too small to be interpreted. Therefore, we believe that the formation of a bimolecular substrate–reagent complex that is strongly regulated by steric factors is the rate-



Scheme 3

dominating process in these reactions. This postulate sounds quite reasonable, since the values of second-order rate constants k_2 and of activation entropies $\Delta S^{\#}$ correlate with the bulkiness of substituents on the target phenols. The steric barriers to the approach of reagent **2** to phenol are much greater in the case of bulky *tert*-butyl substituents than of methyl groups; therefore, k_2 as well as $\Delta S^{\#}$ should decrease from 2,4,6-trimethylphenol, through 2,6-di-*tert*-butyl-4-methylphenol to 2,4,6-tri-*tert*-butylphenol.

EXPERIMENTAL

1-Fluoro-4-chloromethyl-1,4-diazoniabicyclo[2.2.2]octane bis(tetrafluoroborate) (**2a**, Selectfluor™, F-TEDA-BF$_4$) and 1-fluoro-4-hydroxy-1,4-diazoniabicyclo-[2.2.2]octane bis(tetrafluoroborate) (**2b**, Accufluor™, NFTh) were obtained from commercial sources and, for synthetic application, used as received. For kinetic measurements the F-TEDA-BF$_4$ was crystallized from an acetonitrile–methanol mixture and dried under reduced pressure before use. 2,4,6-Tri-*tert*-butylphenol, 2,6-di-*tert*-butyl-4-methylphenol and 2,4,6-trimethylphenol from commercial sources were purified by crystallization; acetonitrile was purified by distillation and stored over molecular sieves. KI and a standard solution of $Na_2S_2O_3$ from commercial sources were used as received.

Reactions of hindered phenols with F-TEDA-BF$_4$ or NFTh

To a solution of 5 mmol of substrate in MeCN or MeCN–NuH mixture (50 ml), 1.95 g (5.5 mmol) F-TEDA-BF$_4$ or 1.76 g (5.5 mmol) NFTh were added and the reaction mixture stirred at 30 °C until KI starch paper showed the reagent to be consumed (3–6 h). The solvent was removed under reduced pressure, the crude reaction mixture dissolved in CH_2Cl_2, and insoluble material filtered off. The solution was then washed with water, dried over Na_2SO_4, and the solvent evaporated. The isolated crude reaction mixtures were analysed by ^{1}H and ^{19}F NMR and thin-layer chromatography, and pure products were obtained after flash chromatography over SiO_2. The spectroscopic data for the known compounds were in agreement with the literature, and unknown products were fully characterized.[7]

Determination of reaction order and rate constants for reactions of hindered phenols with F-TEDA-BF$_4$

Various amounts (0.9, 1.2 and 1.5 mmol) of target phenols were dissolved in 40 ml of acetonitrile or MeCN–NuH mixture, thermostatically controlled at 15 °C. To each solution 0.6 mmol F-TEDA-BF$_4$ dissolved in 20 ml of acetonitrile, thermostatically controlled at 15 °C, was added and the reaction mixtures further stirred at 15 °C. The progress of consumption of F-TEDA-BF$_4$ was monitored by iodometric titration.

At different time intervals, aliquots of 10 ml were pumped off from the thermostatic reaction mixtures, and treated with 20 ml of 0.02 M KI and the liberated iodine was titrated with 0.05 M $Na_2S_2O_3$. The consumption of F-TEDA-BF$_4$ followed a simple second-order rate equation [Eqn. (1)], and the second-order rate constants k_2 collected in Table 1 were determined as the slope of the correlation plot [Eqn. (2)], which always gave a straight line with a correlation coefficient higher than 0.98.

$$\ln(c_{\mathrm{B0}}c_{\mathrm{A}}/c_{\mathrm{A0}}c_{\mathrm{B}})/(c_{\mathrm{A0}} - c_{\mathrm{B0}}) = k_2 t \qquad (2)$$

In Eqn. (2), c_{A0} and c_{B0} are the initial concentrations of the reagent (F-TEDA) and the substrate (phenol) respectively; c_{A} and c_{B} are the concentrations of the reagent and substrate respectively after time *t*. The effect of solvent polarity on reaction rate was evaluated using the Grunwald–Winstein[13] correlation (3) of k_2 with solvent ionizing power Y:

$$\log k_2 = mY + \log k_0 \tag{3}$$

This gave a straight line with a correlation coefficient better than 0.98 and slope $m = -0.18$ for the reaction of **1b** and $m = -0.08$ for the reaction of 2,4,6-trimethylphenol (Table 2). The values for k_2 collected in Tables 1 and 2 are averages from at least three measurements, with no more than 3% relative error.

Determination of the thermodynamic parameters of the transition state for the reaction of hindered phenols with F-TEDA-BF$_4$

Second-order reaction constants k_2 for the reactions of target phenols with F-TEDA-BF$_4$ at different reaction temperatures were measured as described above. The correlation of k_2 with temperature derived from the Eyring equation

$$\ln(k_2/T) = \ln(k_\mathrm{B}/h) + \Delta S^{\#}/R - \Delta H^{\#}/RT \tag{4}$$

was found to be a straight line with a correlation coefficient better than 0.98. The free energy of activation $\Delta G^{\#}$ was calculated from the relation

$$\Delta G^{\#} = \Delta H^{\#} - T\Delta S^{\#}$$

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