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Mechanistic studies and quantification of the electrophilicity of aromatic triflones in σ-complexation and S_NAr reactions

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ABSTRACT

The reactions of anilines (N-nucleophiles) and enamines (C-nucleophiles) with NO_2 and SO_2CF_3 substituted aromatic triflones were investigated spectrophotometrically in acetonitrile at 20 °C. We found that the second-order rate constants k_1 related to the C–N and C–C bond forming step of these nucleophilic aromatic substitution reactions (S_NAr) and σ-complexation reactions follow the three-parameter equation log $k_{(20\,^\circ C)} = s_N(N + E)$, allowing the determination of the electrophilicity E of such aromatic triflones for the first time. The ranking of these neutral electron-deficient compounds on the comprehensive electrophilicity scale defined by Mayr et al. reveals that the most electrophilic triflone, the 1,3,5-tris(trifluoromethanesulfonyl)benzene (TTSB), has an electrophilicity higher than that of the 1,3,5-trinitrobenzene (TNB) the common reference aromatic electrophile in anionic σ-complexation chemistry, by roughly 6 units of E. This finding holds promise for expanding the range of coupling reactions which can be envisioned between this series of electron-deficient neutral aromatics and nucleophiles.

1. Introduction

The reactions of electron-deficient arenes and heteroarenes substituted by very strong electron-withdrawing substituents such as SO_2CF_3 with O-, N- and C-nucleophiles are of great interest from a synthetic and mechanistic point of view [1–7]. Indeed the anionic Meisenheimer σ-complex intermediates are highly stabilized by the SO_2CF_3 substitutents and can be characterized or isolated, and the resulting products are highly valuable aromatic compounds [8–12].

Discussions of the substituent effects and of the mechanisms of these S_NAr type reactions through the use of empirical linear free-energy relationships is one of the preferred approach in the literature. Indeed, since the introduction of the electrophilicity and nucleophilicity concepts to describe the reactivity of electron-deficient (electrophile) and electron-rich (nucleophile) species by Ingold in the 1930s [13], there has been a growing interest in classifying molecules within scales of electrophilicity/nucleophilicity. From that time, the classification and the quantification of the reactivity organic molecules within empirical and hopefully unique scales of electrophilicity and nucleophilicity have been attempted. For instance, several linear free-energy relationships (LFERs) such as the well-known Hammett equation [14] and other relationships involving kinetic parameters instead of equilibrium constants have been proposed in the literature [15–19]. The main objective of such correlations was the development of absolute reactivity scales that could be independent on the reactivity of the nucleophile/electrophile partners. This objective is ambitious if one considers that a universal scale should accommodate a wide diversity of chemical species presenting quite different structural and bonding properties.

Mayr and co-workers have, however, recently defined nucleophilicity and electrophilicity parameters that are independent of the reaction partners and that describe the rates of many reactions in organic and organometallic chemistry [20–23]. It has been well established, in contrast to the accepted opinion about the relative character of the experimental electrophilicity/nucleophilicity scales, that the rates of reactions of hundreds of carbenium ions, Michael acceptors and other electrophiles with charged and uncharged σ-, π- and n- nucleophiles obey the linear free-energy relationship given by:

$$\log k_{(20\,^\circ C)} = s_N(N + E) \qquad (1)$$

where $k_{(20\,^\circ C)}$ is the second-order constant in $mol^{-1}\,dm^3\,s^{-1}$, s_N is the nucleophile sensitivity parameter, N is the nucleophilicity parameter, and E is the electrophilicity parameter. Based on Eq. (1),

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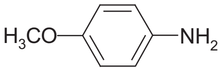
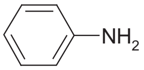
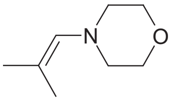
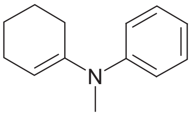
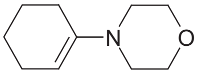
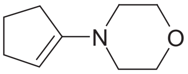
Table 1
Nucleophilicity N and nucleophile sensitivity parameter s_N of the anilines **A**–**C** and of the enamines **D**–**G** used as reference nucleophiles in this study.

	Nucleophiles	N	s_N
A		13.42[a]	0.73[a]
B		13.19[a]	0.69[a]
C		12.64[a]	0.68[a]
D		10.04[b]	0.82[b]
E		10.73[b]	0.81[b]
F		11.40[c]	0.83[c]
G		13.41[b]	0.82[b]

[a] From Ref. [29].
[b] From Ref. [30].
[c] From Ref. [22].

general electrophilicity (E) and nucleophilicity (N) scales, each covering a reactivity range of more than 30 orders of magnitude have been defined and successfully used to predict the feasibility and rate of many interactions [24–27].

Interestingly, it has recently been shown that the electrophilicity of an extended series of neutral electron-deficient nitroaromatics and heteroaromatics of widely differing reactivity and structure is appropriately described by this equation [28].

In this paper, we report on the determination of the electrophilicity of the four aromatic triflones **1**–**4** shown in Scheme 1. Electrophilicity parameters E of **1**–**4** were determined from the kinetics of their reactions with various anilines and enamines **A**–**G** of known nucleophilicity parameters N and which are defined as reference nucleophiles (Table 1). This extension of the applicability of Eq. (1) to S_NAr and σ-complexation processes further demonstrates the general utility of this relationship and the new kinetic data might allow synthetic chemists to design new addition reactions of nucleophiles to NO_2 and SO_2CF_3 substituted arenes.

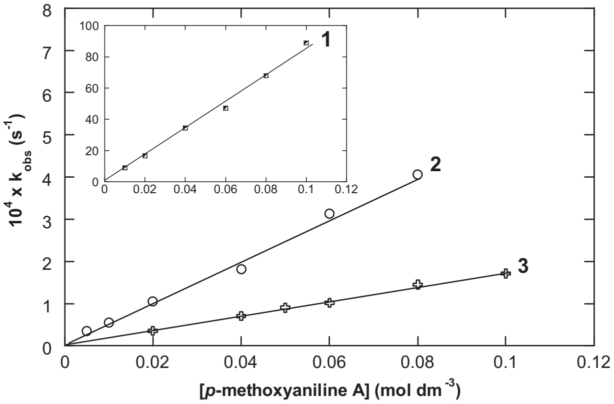


Fig. 1. Influence of the concentration of p-methoxyaniline **A** on the observed first-order rate constant for addition to 2,4,6-tris(SO_2CF_3)anisole 1, 2,6-bis(SO_2CF_3)-4-nitroanisole 2, and 4,6-bis(SO_2CF_3)-2-nitroanisole **3** in MeCN at 20 °C.

2. Results and discussion

The kinetic study was performed under pseudo-first-order conditions with the concentration of anilines or enamines in excess over the substrates concentration. All of the reactions obeyed first-order kinetics. Pseudo-first-order rate constants (k_{obs}) were calculated from the equation $\ln(A_\infty - A_t) = -k_{obs}t + C$. The k_{obs} values with the reaction conditions are summarized in Tables S1–S7 in the Supporting Information.

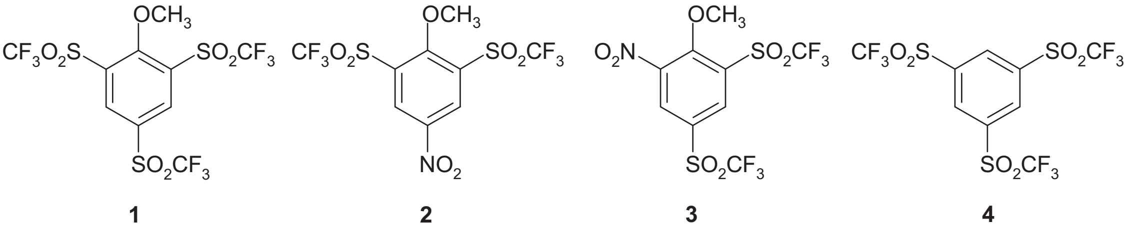
For anilines reactions, all pseudo-first-order rate constants k_{obs} obey Eq. (2) with negligible k_o as illustrated in the plots of k_{obs} *vs.* aniline concentration in the case of the reaction of the p-methoxyaniline **A** with the triflones **1**, **2** and **3** (Fig. 1). The second-order rate constants k_1 were determined from the slopes of theses linear plots, based on Eq. (2).

$$k_{obs} = k_o + k_1[\mathrm{An}] \tag{2}$$

Furthermore, no higher-order terms were detected and no complications were found in the determination of k_1.

This suggests that there is no base catalysis or noticeable side reactions, and that the overall reaction follows the mechanism described in Scheme 2. This is also in agreement with the traditional interpretation of nucleophilic aromatic substitution by amines, and in agreement with the S_NAr–Ad. E mechanism, where the rate-limiting formation of the zwitterionic σ-complex intermediate **ZW**$^\pm$ is followed by the fast expulsion of the methoxy leaving group [31,32].

The second-order rate constants k_1 of the S_NAr reactions of anilines **A**–**C** (p-methoxyaniline **A**, p-methylaniline **B** and aniline **C**) with aromatic triflones **1**–**3** at 20 °C in MeCN are summarized in Table 2. The substitution of one nitro group of 2,6-bis(SO_2CF_3)-4-nitroanisole **2** and 2,4-bis(SO_2CF_3)-6-nitroanisole **3** by a SO_2CF_3 group to give the 2,4,6-tris(SO_2CF_3)anisole **1** increases the rate of reactions with anilines by 15 and 40-fold, respectively. These results emphasize that the SO_2CF_3 group has a stronger electron-withdrawing character than a NO_2 group, both in the *ortho*- and *para*-positions of a reactive center in an aromatic ring. This behavior is consistent with the higher values of the Hammett constants of the SO_2CF_3 substituent ($\sigma_m = 0.76$, $\sigma_p = 0.96$,



Scheme 1. Structures and numbering of the aromatic triflones.